"NOTICE: When Government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the U.S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto."

ENGINEERING AND INDUSTRIAL EXPERIMENT STATION

College of Engineering

University of Florida

Gainesville

OOR FINAL REPORT

THE EFFECT OF FOREIGN SUBSTANCES ON THE STRENGTH OF POWDER-METAL AGGREGATES

Department of Mechanical Engineering
Engineering and Industrial Experiment Station
University of Florida

September 30, 1958

OOR Project No. 1423
Contract No. DA-01-009-ORD-439

TABLE OF CONTENTS

ABSTRACT

The work described in the body of this report was aimed at revealing more knowledge of the properties of metal-oxide mixtures produced by the methods of powder metallurgy. This study is one of several, inaugurated since the work of Irmann, that have been concerned with the evaluation of the effect of a dispersed oxide phase in a metal matrix on the properties of the resultant material.

The report is divided in four parts, each dealing with a different pure metal. The metal matrices covered are copper, titanium, zirconium, and iron. The oxides were introduced by mixing the pure oxides with the pure metal powders. For each metal a program was devised to determine the optimum conditions of particle size, method of aggregation, pressing pressure, sintering atmosphere and temperature and additional pressing and sintering operations. The criteria used were density and hardness. Both cylinders and tensile bars were evaluated.

The oxide added to copper was titania. This oxide was also used as the dispersed phase in titanium; to minimize oxide solubility, low temperature sintering was used with tin as the bonding agent. Zirconia was added to zirconium; both hydride zirconium and high purity zirconium metal were used, but in both instances the resultant products were very brittle.

The greatest amount of work was done with carbonyl iron. The oxides added included zirconia, thoria, ceria, lanthana, neodymia, dysprosia, and gadolinia. Lanthana was found to prevent bonding of the iron matrix, while the other oxides were found to be only

slightly embrittling. The iron - gadolinia mixture offers considerable promise for a control rod material in nuclear applications.

In general, the oxide additions to each metal investigated resulted in increased hardness and strength at elevated temperatures.

INTRODUCTION:

The investigations of von Zeerleder (Modern Metals 8(1953)40) and of Irmann (Rev. Aluminum 28(1951)267) on sintered aluminum powder (SAP) have attracted a great deal of attention. Cylinders made from unalloyed aluminum powder containing up to 20% oxide have been shown to possess creep strengths at 500-900°F almost four times greater than those of wrought aluminum alloys.

Gregory and Grant (Trans. AIME 200(1954)247) have attributed this strengthening to a very fine dispersion of oxide particles. Their short-time test results exhibited a correlation with the reciprocal of the particle spacing (0.35 to 2 microns). It is believed that the dispersed phase hindered recrystallization of the metal matrix and acted as a barrier to the passage of dislocations.

Other metals, also, may be strengthened by oxide bonding. Furthermore, the oxide bonding may be achieved in a variety of ways. It is possible to strengthen certain iron powder parts by sintering them in a steam atmosphere. In this case, the oxide phase is produced by reaction with the water vapor that has penetrated through the pores of the pressed compact. The writer of this proposal has observed the very pronounced hardening of graphite-bronze powder compacts when sintered in air as contrasted to the very soft structures produced when they were sintered in hydrogen, or in a vacuum. Clasing and Sauerwald (Z. anorg. u. allgem. Chem. 271(1952)88) found an improvement in strength of 25-30% in compacts made from artifically oxidized copper powder. Iron oxide films formed on particles of iron also resulted in an improvement

of strength in the compact. In the fine powder (20 microns and finer) used for the aluminum high-temperature-strength product the oxide film is formed naturally on the grains.

These methods limit the oxide or oxides introduced to that or those of the metal or some constituent of an alloy (e. g. Cd in a Ag-Cd alloy). A wide variety of metal-oxide bonds may be had, however, by adding oxides to the metal powder. This has been achieved with aluminum (author's unpublished work) and with molybdenum (AD-24541). In most cases an improvement of high temperature properties was secured. The addition of oxides in limited quantities to metal powders to improve the high temperature properties of the parts produced therefrom is a relatively old art (Jeffries and Archer, The Science of Metals, McGraw-Hill, 1924, 106, and Goetzel, Treatise on Powder Metallurgy, III, Interscience, 1952, 640).

The purpose of this work is to study the strengthening effects of various metal oxides added to copper, titanium, zirconium, and iron.

PART I

COPPER POWDERS

INTRODUCTION:

The first stage of this study was the determination of the optimum combination of particle size, aggregate conditions, pressing pressure, and sintering temperature for the production of a sintered compact with maximum density and uniform physical properties. The second stage was concerned with the effect of foreign substances on the properties of this matrix product.

MATERIALS:

The first phase of this study was carried out on copper powders since they were obtainable in high purity over a variety of particle sizes, and, among the industrially important metals, offered a minimum of difficulty in pressing and in sintering.

Copper powders were obtained from three different sources, covering a wide range of particle sizes. The sources are:

Belmont Smelting and Refining Works, Inc.
Metals Disintegrating Company, Inc.
United States Metal Refining Company

Descriptions, mesh sizes and chemical compositions of these powders are given in Table I, and photomicrographs of some of the particles are given in Figure 1.

The titanium dioxide (Anatase) was National Formulary grade, purchased from H. Kohnstamm and Company, Inc.

The tin powder, obtained from the McGean Chemical Company, had the following specifications:

Pure virgin straits tin 99.8% Sn
Screen Analysis: 94% -325
6% -200 + 325

APPARATUS:

Pressing Dies

The pressing of cylindrical powder-metal compacts was done in a hardened steel die having a cylindrical cavity of 1.25 inches diameter and 3 1/8 inches length. An annular ring of soft steel of 4 inches diameter was shrunk over this die to place the carburized walls of the bushing portion in compression and prevent their splitting under high pressing pressures. Pressures of over 100 tons per square inch were attained.

Figure 2a shows the die in place on the 150-ton-capacity press used in this work. Also shown is the block used for ejection.

A special double acting die was used to press the tensile test bars as specified by the Metal Powder Association Standards (Figure 2b).

Sintering Furnace

A schematic drawing is presented in Figure 3; a general view of the apparatus is shown in Figure 4. Not shown are the temperature controllers for the furnaces. Figure 5 is a close-up of the quartz-tube sintering chamber, and Figure 6 is a view of the vacuum equipment. The furnace closest to the mechanical vacuum pumps was used for the purification of the hydrogen and contains titanium turnings. The adjacent furnace was used for hydrogen reduction of the powders. Only enough powder for a given run of samples was reduced at a time. If it was not used immediately, the reduced powder was stored in a hydrogen atmosphere.

All of the intricate glass work was done by the glass blower of the College of Engineering, Mr. E. C. Logsdon.

Hot Hardness Tester

The sintered tensile bars were tested for hot hardness using the Hot Hardness Test Furnace (Figure 7), especially designed to fit the Model 4JR Rockwell Hardness Tester. A special high temperature resistant, diamond brale, mounted on a precision ground spindle, was projected into the furnace chamber, where the sample could be placed on the stainless steel block and readings taken. The bottom of the furnace was water cooled. A specimen thermocouple and a control thermocouple in conjunction with a controller were used to record and control the temperature. The test bar could be directly observed in the furnace by using an inclined mirror. A one pound load was used; this particular scale was named the "I" scale. To get an average reading, a few readings were usually taken at one particular temperature, the speed of a dashpot being previously adjusted to a moderate rate of loading.

Creep Testing Machine

Creep data were taken at 15,000 lb/in^2 stress, i.e., about one-half the breaking stress for best specimens, and at a temperature of $600^{\circ}F$. The Creep Testing Machine (Figure 8) was a constant load, variable extension unit.

PROCEDURE AND RESULTS.

Cylindrical Compacts

The first-used procedure consisted of blending various-sized powders and aggregating the mix by milling with xylene. The use of the "moist" powder precluded the entrapping of air in the compact at the higher pressing pressures.

Specimen dimensions vary according to processing conditions; but an average specimen weighed 25 grams and was a cylindrical slug of approximately 1.25 inches diameter. Density was determined by the weight-volume method after the specimens had been machined flat to 0.001 inch and ground on the diameter. Hardness was measured by the specially devised "J" scale. In this scale a one pound weight was used on the lever system of a Model 4JR Rockwell Tester and the indenter was a 1/8 inch diameter steel ball. A conversion table for Rockwell "J" to Brinell, 500 gr., was developed.

As Received Condition -- The powders were first evaluated in the condition as received from the metal supplier. Cylindrical specimens, 1 1/4 inch in diameter and 35 grams in weight, were formed under pressures varying from 15 to 75 tons per square inch, in 15 ton increments. They were then sintered 4 hours at 700°C, in a helium atmosphere. The green and sintered densities of compacts made from the four powders and their hardness values are given in Table II.

The green density increased in a regular fashion with pressure for the three powders. The coarser the powder the greater the green density for any given pressure. Density measurements were made by the weight-volume method. For MD 105and MD 151 powders pressed at 15 t.s.i., sintering for 4 hours at 700°C resulted in an increase in density. At 30 t.s.i., there was no change in density upon sintering, and for all higher pressures the density decreased upon sintering. The coarse powder, USMRC,

showed a decrease in density upon sintering for all pressures. Because of the xylene used in pressing the flake powder, density determinations were not made on the green compacts.

The fine powders yielded "bubbled" compacts upon sintering after pressing above 45 t.s.i. No bubbles were produced in the compacts made from the coarse powder. One attempt to eliminate the bubbles was to briquette at 15 t.s.i., sinter one hour at 425°C in a helium atmosphere, repress at a series of higher pressures, and resinter four hours at 700°C in a helium atmosphere. The data are given in Table III. This procedure had no effect; bubbling still occurred after sintering in compacts pressed over 45 t.s.i.

The next attempt to prevent bubbling was to exclude the entrapped air by pressing powders that had been moistened with xylene. Furthermore, an attempt was made to control porosity by mixing powders of different particle sizes. Just enough xylene was blended with the powders to permit them to cohere as nodules upon being forced through a 20 mesh sieve. During pressing, the xylene was squeezed out, preventing any air from being entrapped. The pores were filled with xylene however, and while most of this was volatilized during sintering, some remained in the compacts. This procedure eliminated bubbling, but did not yield a high sintered density. The data of Table IV give the density and hardness of compacts made from several powder blends.

Hydrogen-Reduced Condition -- Upon completion of the evaluation of the powders in the as-received condition, a program to evaluate the oxide-free powders was begun. Table V gives the

sintered density and hardness values of compacts made from hydrogen-reduced powders, nodularized with xylene. The presence of the xylene during pressing precluded the formation of bubbles during sintering. High density and hardness values were obtained. An attempt was made to densify the compacts by hammering, but their ductility was too low and cracking occurred.

It was thought that vacuum annealing would prevent bubbling during sintering of pressed powders. The data of Table VI show that vacuum sintering alone will not remove the air entrapped in compacts made from fine powders pressed at pressures of 45 t s.i. and higher.

A special processing procedure was devised to eliminate the use of xylene and yet to permit the attainment of high densities. This entailed an initial low pressing pressure of hydrogen-reduced powder, a low-temperature sinter in a hydrogen atmosphere at a pressure below atmospheric, followed by a higher-temperature sinter in vacuo, and repressing at a medium high pressure, and a similar resintering at a high pressure. The results of this treatment are given in Table VII.

Tensile Bars

The optimum pressing and sintering techniques that had been developed for the cylindrical specimen were closely followed in this series of tests . To summarize briefly, the procedure was as follows:

1. Reduction of copper powder in dry Hydrogen at 450°C for 4 hours
2. Mixing of powder with alloying elements
3. Pressing of mixes of 15 t.s.i.

4. Sintering of pressed specimens first for 2 hours at 700°C in partial pressure of H_2 (300-400mm), and then in vacuo at the same temperature or 750°C from 5-17 hours.

5. Samples repressed at 60 t.s.i. and then sintered in exactly the same way as (4).

Each sample, after final sintering, was tested and the properties of the material evaluated. The bars made from the MD 105 powder had the best properties and it was selected as the basis in subsequent studies.

In this series of tests the emphasis was laid on the properties of alloys at elevated temperatures.

In general, the following data were collected:

1. Density of compact
2. Tensile strength
3. Elongation and reduction in area
4. Hot hardness
5. Creep values

TiO_2 (Anatase) was selected as the non-metallic addition in this series of tests. In choosing this particular oxide, consideration was given to its low density and heat resisting properties. The oxide was incorporated into the copper powder by means of a thorough mixing.

Increasing the amount of oxide lowered both the strength and the ductility (Table VIII and Figure 9).

In order to improve the tensile strength, a fixed amount of tin (7%) was added to the mixture of copper powder and TiO_2. The samples were tested for hot hardness, and the data are given in Table IX and in Figure 10. An identical set of tensile bars was tested for creep, and the data are given in Table X.

TABLE 1

Data on Copper Powders

Description	Mesh Size, In Percent of Fraction				Chemical Composition (Qualitative Spectrochemical Analysis)
	+100	+200	+325	-325	
Belmont #250 Flake					Iron, Zinc 0.01 to 0.1% (each)
MD 105	-	0.1	0.9	97.0	Tin, Iron 0.03 to 0.3% (each) Aluminum, Silicon, Lead, Zinc, Calcium 0.01 to 0.1% (each)
MD 151	0.1	16.3	25.6	58.0	Tin, Iron 0.03 to 0.3% (each) Aluminum, Silicon, Lead, Zinc, Calcium 0.01 to 0.1% (each)
USMRC "O"	70	30			Iron, Zinc 0.01 to 0.1% (each)

TABLE II

Density and Hardness of Compacts Made From As-Received Powders

Powder	Pressing Pressure	Green Density (as pressed)		Sintered Density (4 hours at 700°C in helium)		Sintered Hardness	
	t.s.i.	gr/cc	% of theor.	gr/cc	% of theor.	J scale	Brinell (conv.)
MD 105 fine	15	6.14	68.5	6.38	71.0	100	16
	30	7.26	81.0	7.24	81.0	111	43
	45	7.81	87.0	7.58	84.5	115	53
	60	8.04	90.0	7.39	82.5	113	48
	75	8.20	91.5	7.13	79.5	112	45
	15/75	8.23	92.0	7.23	81.0	-	-
MD 151 medium fine	15			6.64	74.0	100	16
	15	6.53	73.0	6.63	74.0	99	14
	30	7.67	85.5	7.67	85.5	113	48
	30	7.67	85.5	7.67	85.5	114	50
	45	8.12	90.5	7.90	88.5	113	48
	45	8.22	92.0	7.92	88.5	115	53
	60	8.49	95.0	7.76	86.5	112	46
	60	8.45	94.5	7.84	87.5	114	60
	75	8.61	96.0	7.71	86.0	110	39
	75	8.54	95.5	7.84	87.5	111	43
USMRC coarse	15	6.85	76.5	6.82	76.0	100	16
	15	6.80	76.0	6.60	61.5	70	-
	30	7.88	88.0	7.58	83.5	107	30
	30	7.89	88.0	7.54	83.0	93	-
	45	8.39	93.5	7.90	88.0	110	39
	45	8.35	93.5	7.80	87.0	98	12
	60	8.60	96.0	7.98	89.0	109	35
	60	8.60	96.0	7.94	88.5	102	19
	75	8.76	98.0	8.02	89.5	105	26
	75	8.70	97.0	7.95	89.0	108	33
Belmont #250; flake agglomerated with xylene	15			7.68	86.0		
	30			7.75	86.5		
	45			7.74	86.5		
	60			7.95	89.0		
	75			7.85	88.0		

TABLE III

Effect of Briquetting on Density

Powder: MD 105 - fine, as-received condition

Initial Pressure	Green Density (as pressed)		Density after sintering 1 hour at 425°C in He, and pressing as shown			Density after sintering 4 hours at 700°C in He	
t.s.i.	gr/cc	% of theor.	Pressure t.s.i.	gr/cc	% of theoretical	gr/cc	% of theoretical
15	6.20	69.0	15	6.37	71.0	6.52	73.0
15	6.14	68.5	30	7.30	81.5	7.35	82.0
15	6.19	69.0	45	7.83	87.5	7.59	85.0
15	6.12	68.5	60	8.10	90.5	7.41	83.0
15	6.16	67.0	75	8.19	91.5	7.29	81.5

TABLE IV

Effect of Blending and Nodularizing Powders in the As-Received Condition on the Density of Compacts

Powder	Pressing Pressure	Green Density (as pressed)		Density after Sintering 4 hours at 700°C, in He		Sintered Hardness	
	t.s.i.	gr/cc	% of theoretical	gr/cc	% of theoretical	J scale	Brinell (conv.)
MD 105, fine, nodularized with 15% xylene	45			7.25	81.0	110	39
	60			7.84	87.5	116	56
	75			7.84	87.5	117	64
MD 105, fine, 75%: USMRC, coarse, 25%, nodularized with 12% xylene	45	7.61	85.0	7.55	84.5	111	42
	60	8.10	90.5	7.74	86.5	113	48
	75	8.20	91.5	7.64	85.5	113	48
MD 105, 50%: USMRC, coarse, 50%, nodularized with 10% xylene	45	8.03	89.5	7.82	87.5	111	42
	60	8.24	92.0	7.85	87.5	111	42
	75	8.20	91.5	7.93	88.5	112	44
MD 105, fine, 25%: USMRC, coarse, 75%, nodularized with 5% xylene	45	8.20	91.5	7.85	87.5	106	28
	60	8.40	94.0	8.01	89.5	108	33
	75	8.43	94.0	7.98	89.0	108	33

TABLE V

Densities of Compacts from Hydrogen-Reduced and Nodularized Powders

Pressing Pressure	Sintered Density 4 hours at 700°C in He		Density of Sintered Specimens after Cold Reduction of 20% by Hammer and Resintering 2 hours at 900°C in hydrogen		Sintered Hardness 4 Hours at 700°C in Helium	
t.s.i.	gr/cc	% of theoretical	gr/cc*	% of theoretical	J Scale	Brinell (conv.)
(Powder MD 105-fine, reduced in hydrogen 1 hour at 335°C, moistened with xylene, agglomerated)						
45	7.80	87.0	7.87	81.0	116	56
60	8.03	89.5	7.31	81.5	119	71
75	8.10	90.5	7.08	79.0	119	71
100	8.07	90.0	7.13	79.5	119	71
(Powder MD 151-medium fine, reduced in hydrogen 1 hour at 335°C, moistened with xylene, agglomerated)						
45	7.93	88.5	7.60	85.0	112	44
60	8.21	91.5	7.57	84.5	115	53
75	8.23	92.0	7.52	84.0	116	56
90	8.21	91.5	7.60	85.0	115	53

* Determined by Archimedes Method.

TABLE VI

Effect of Vacuum Sintering on Density

Powder: MD 105; fine, reduced in H_2, 2 hours at 475°C

Pressing Pressure	Green Density (as pressed)		Density after Sintering 3 hours at 480°C and 2 hours at 700°C, in vacuo		Sintered Hardness	
t.s.i.	gr/cc	% of theoretical	gr/cc	% of theoretical	J Scale	Brinell (conv.)
30	7.50	84.0	7.72	86.5	117	64
45	8.00	89.5	bubbles	-	-	-
60	8.27	92.5	bubbles	-	-	-
75	8.48	95.0	bubbles	-	-	-

TABLE VII

Schedule of Special Processing for High Density

Powder: MD 105; fine, reduced in hydrogen, 4 hours at 450°C

Treatment	Density		Hardness	
	gr/cc	% of theor.	J Scale	Brinell (conv.)
1) Pressed 30 t.s.i., sintered one-half hour at 700°C, 210 mm absolute pressure H_2, 1 hour at 700°C, in vacuo, 1 micron	7.74 7.60	86.5 85.0		
2) As in 1), then repressed 60 t.s.i	8.40 8.25	94.0 92.0		
3) As in 2), then resintered 2 hours at 480°C, 600 mm absolute pressure H_2, 4 hours at 700°C, in vacuo, 1 micron	8.40 8.25	94.0 92.0	118	66
4) As in 3), then repressed 75 t.s.i.	8.61 8.60	96.0 96.0		
Powder: MD 151; medium fine, reduced in hydrogen, 4 hours at 450°C				
1) Pressed 30 t.s.i., sintered one-half hour at 700°C, 210 mm absolute pressure H_2, 1 hour at 700°C, in vacuo, 1 micron	7.84 7.84	87.5 87.5		
2) As in 1), then repressed 60 t.s.i.	8.58 8.64	96.0 96.5		
3) As in 2), then resintered 2 hours at 480°, 600 mm absolute pressure H_2, 4 hours at 700°C, in vacuo, 1 micron	8.58 8.64	96.0 96.5	117	64
4) As in 3), then repressed 75 t.s.i.	8.79 8.76	98.5 98.0		

TABLE VIII

The Evaluation of the Effect of TiO_2 Additions
On The Mechanical Properties of the Tensile Test Bars

Processing Method	Powder Description and Composition	Density gr/cc	Tensile Strength lb/in^2	Elongation %
Powder reduced at 450°C for 4 hours in H_2 atmosphere. Powder was mixed with TiO_2 and pressed at 15 t.s.i., sintered first in partial pressure of H_2 for 2 1/2 hours at 700°C and then in vacuo for 5 hours at 700°C. Repressed at 60 t.s.i., sintered again, first in partial press of H_2 for 2 1/2 hours at 700°C and then in vacuo for 17 hours at 900°C.	MD 105 Pure	8.58	32900	32
	MD 105 & 1/2% TiO_2	8.56	31040	16
	MD 105 & 1% TiO_2	8.50	30920	13
	MD 105 & 2% TiO_2	8.355	27220	6
	MD 105 & 4% TiO_2	8.15	21520	3
	MD 105 & 8% TiO_2	7.87	15130	3
	MD 105 & 12% TiO_2	7.70	11780	3
	MD 105 & 16% TiO_2	7.35	7390	2

TABLE IX

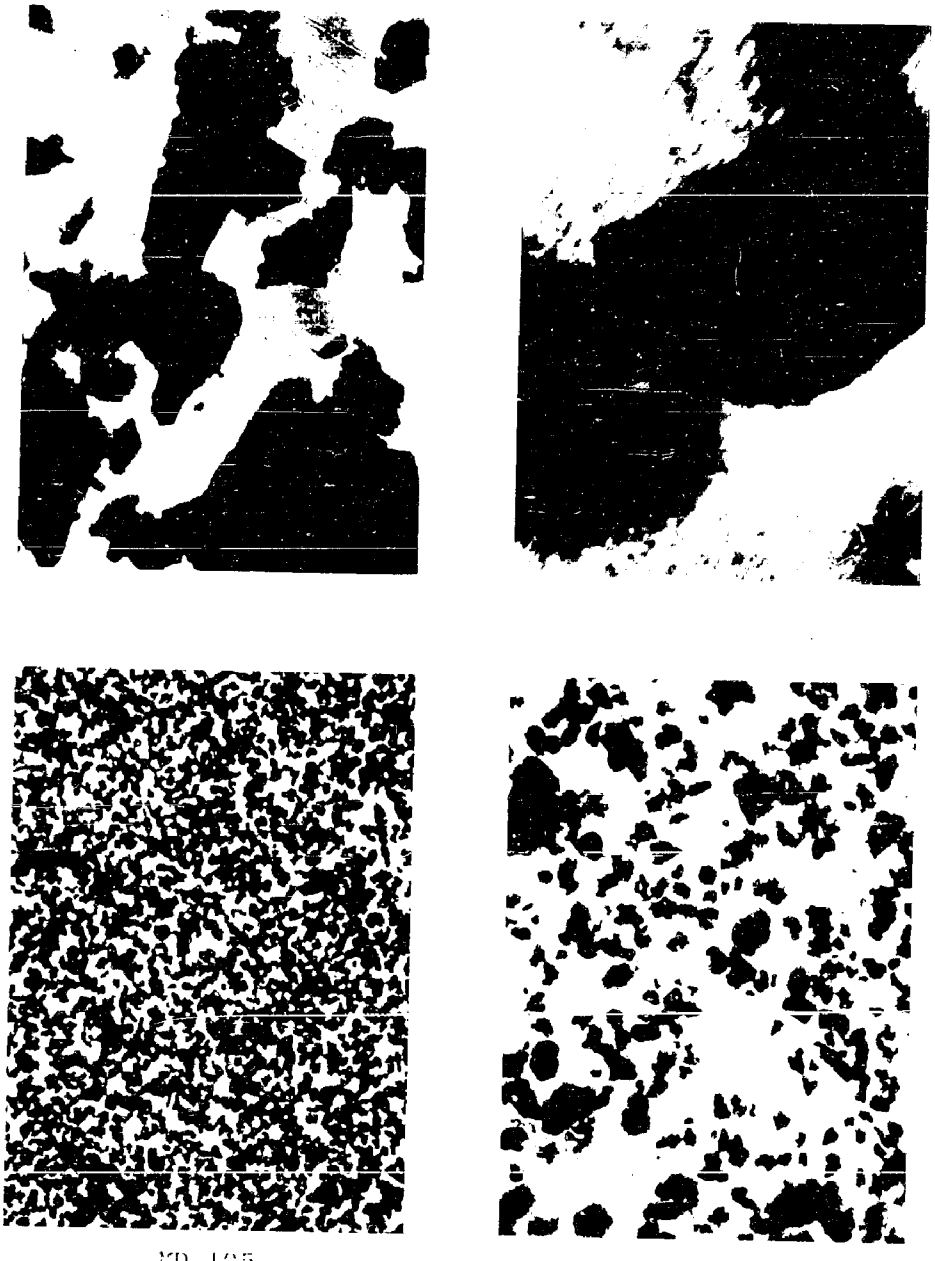
Effect of TiO_2 Additions on the Hot Hardness

Processing Technique	Composition	Temperature of Hot Hardness Reading - I Scale								
Powder reduced at 480°F for 4 hours in H_2 mixed with 7% Sn and TiO_2 and pressed at 15 t.s.i. Presintered at 480°C in partial pressure of H_2 for 1 hour and then sintered in vacuum for 15 hours at 647°C. Samples were repressed at 60 t.s.i. and sintered again, in H_2 for 2 hours and in vacuo for 15 1/2 hours at 750°C.	MD 105 Pure	90 94	200 92.5	340 90	440 90	540 88	630 87	750 84.5	1000 68.5	
	MD 105-7% Sn and 0% TiO_2									
	MD 105-7% Sn and 1/2% TiO_2	90 100	200 100.5	300 100.5	430 99.5	500 99.5	750 94	800 92.5	900 84	1000 77.5
	MD 105-7% Sn and 1% TiO_2	90 101.5	200 100.5	200 99	400 99	500 97.5	825 86.5	900 81	1000 70	
	MD 105-7% Sn and 2% TiO_2	90 101	200 99	300 97.5	400 96	500 96	700 90.5	800 88	900 88	1000 74
	MD 105-7% Sn and 4% TiO_2	90 101	300 100	500 98	600 97	700 93	800 87	900 83	1000 78	

TABLE X

Effect of TiO_2 Additions on the Creep Properties of Pressed MD 105

Processing Technique	Composition (% TiO_2)	Number of Hours at 700°F and 5000 lb/in^2
Powder reduced at 480°F for four hours in H_2. Mixed with 7% Sn and TiO_2 and pressed at 15 t.s.i. Presintered at 480°C in partial pressure of H_2 for 1 hour, then sintered in vacuum for 15 hours at 647°C. Samples were then re-pressed at 60 t.s.i., and then sintered again first in H_2 for 2 hours and then in vacuo for 15 1/2 hours at 750°C	Pure	6.7
	1	8.4
	2	8.2
	4	...
	8	...



MD 165 MD 151

Figure 1

Copper Powders x250

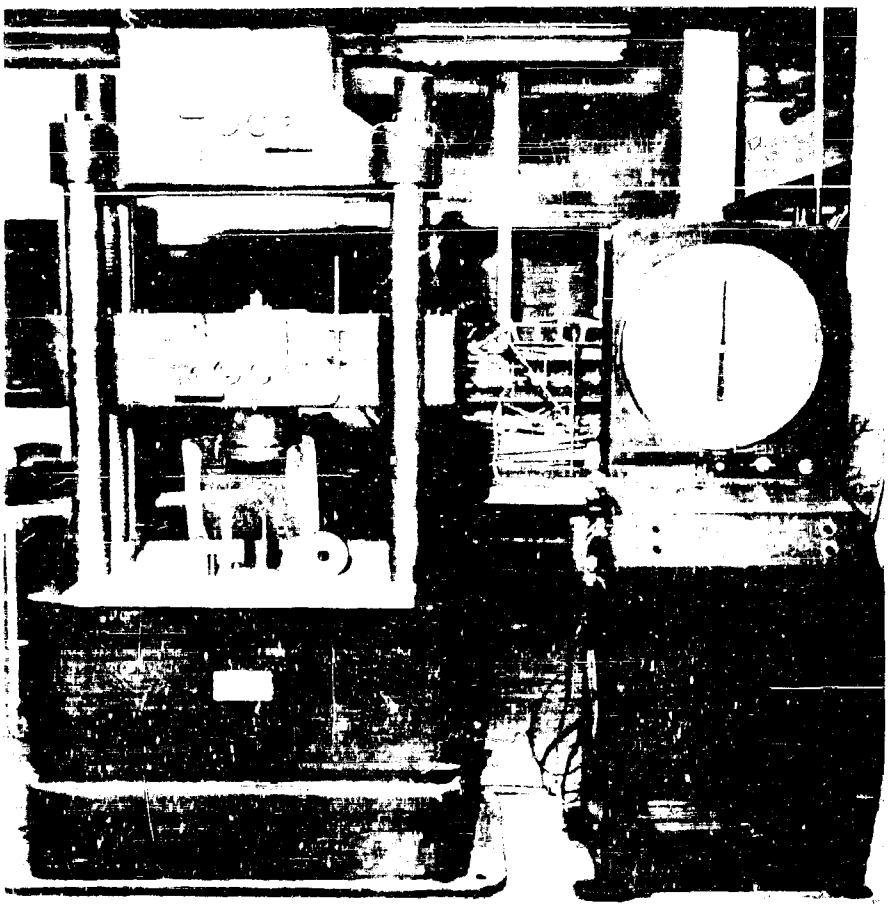


Figure 2a
150 Ton Capacity Press

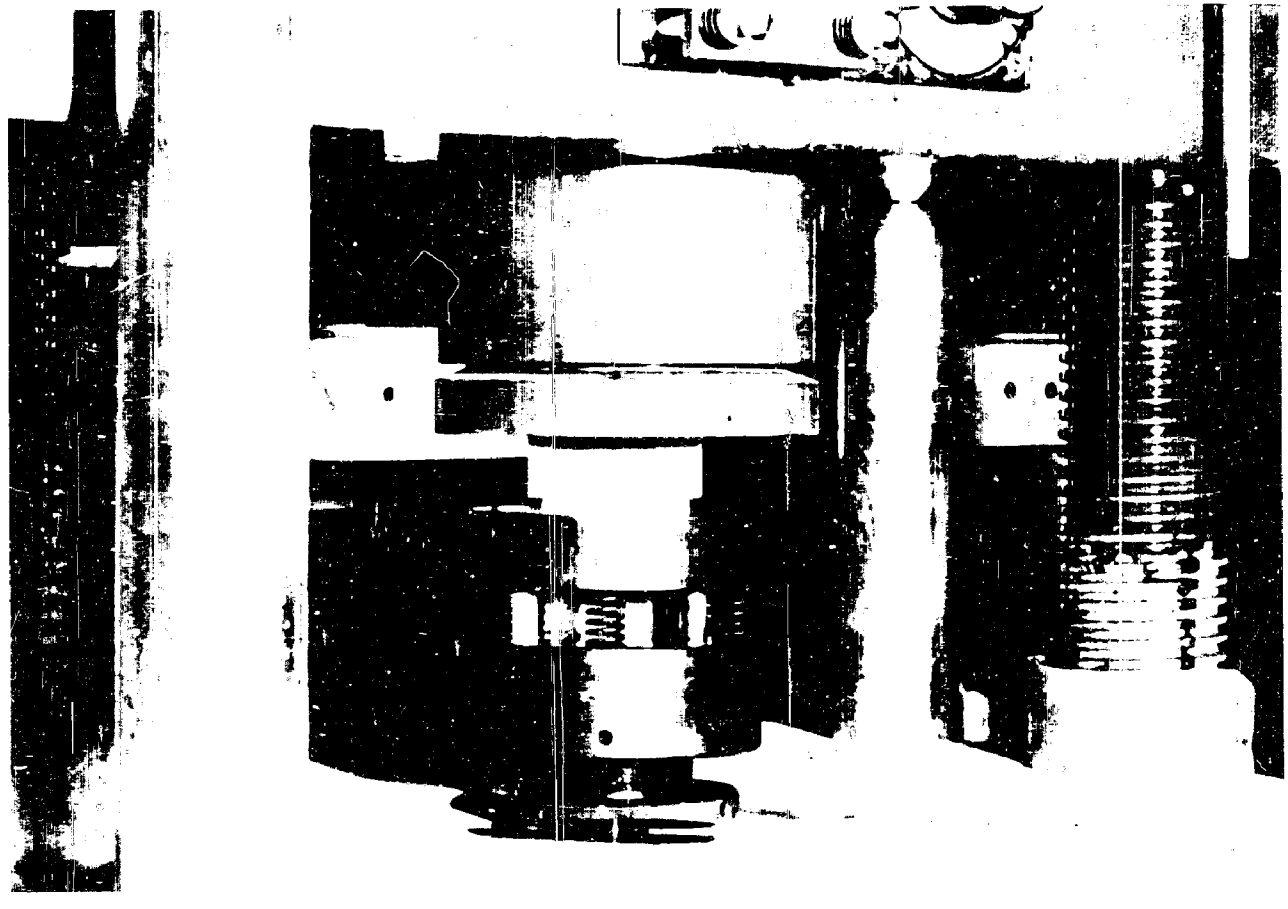


Figure 2b

Doub e Acting Tensile Bar Pressing Die

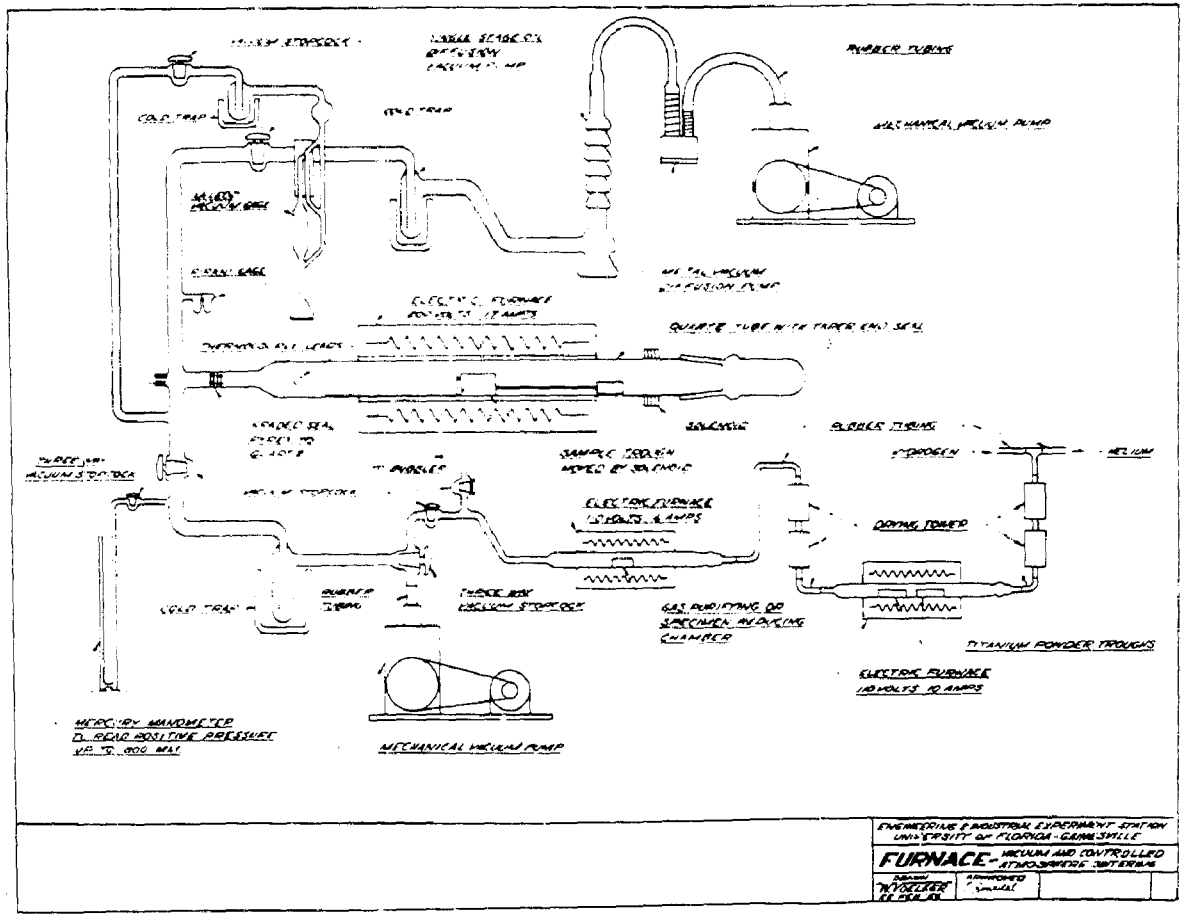

RUBBER TUBING
COLD TRAP
MECHANICAL VACUUM PUMP
ELECTRIC FURNACE
QUARTZ TUBE WITH TAPER END SEAL
SAMPLE HOLDER
BUBBLER TUBING
HYDROGEN
HELIUM
DRYING TOWER
THREE WAY VACUUM STOPCOCK
GAS PURIFYING OR SPECIMEN REMOVING CHAMBER
TITANIUM POWDER TROUGHS
ELECTRIC FURNACE
110 VOLTS 10 AMPS
MERCURY MANOMETER
MECHANICAL VACUUM PUMP
FURNACE- VACUUM AND CONTROLLED ATMOSPHERE

Figure 3

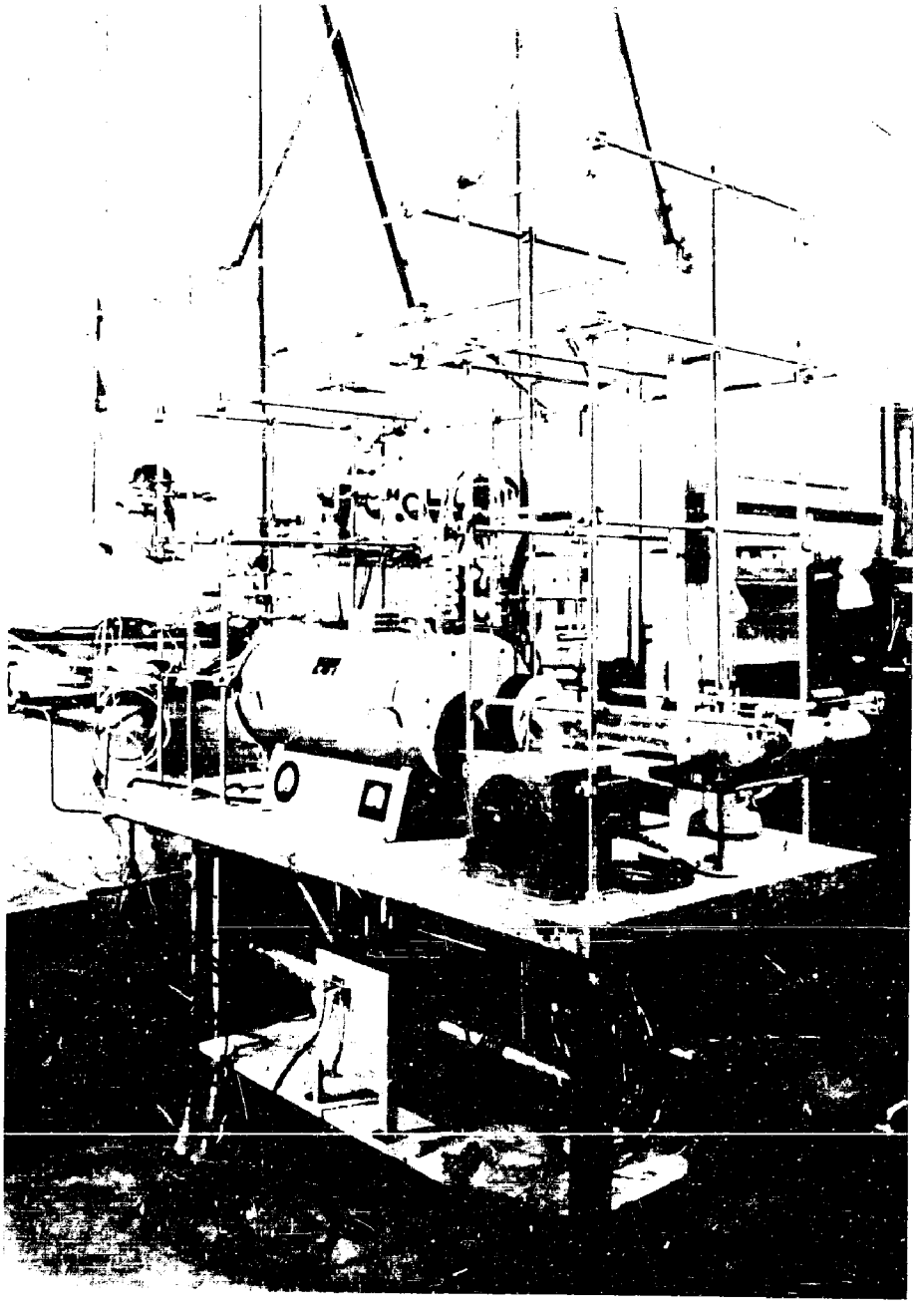


Figure 4

Apparatus for Sintering in Vacuum
and in Controlled Atmospheres

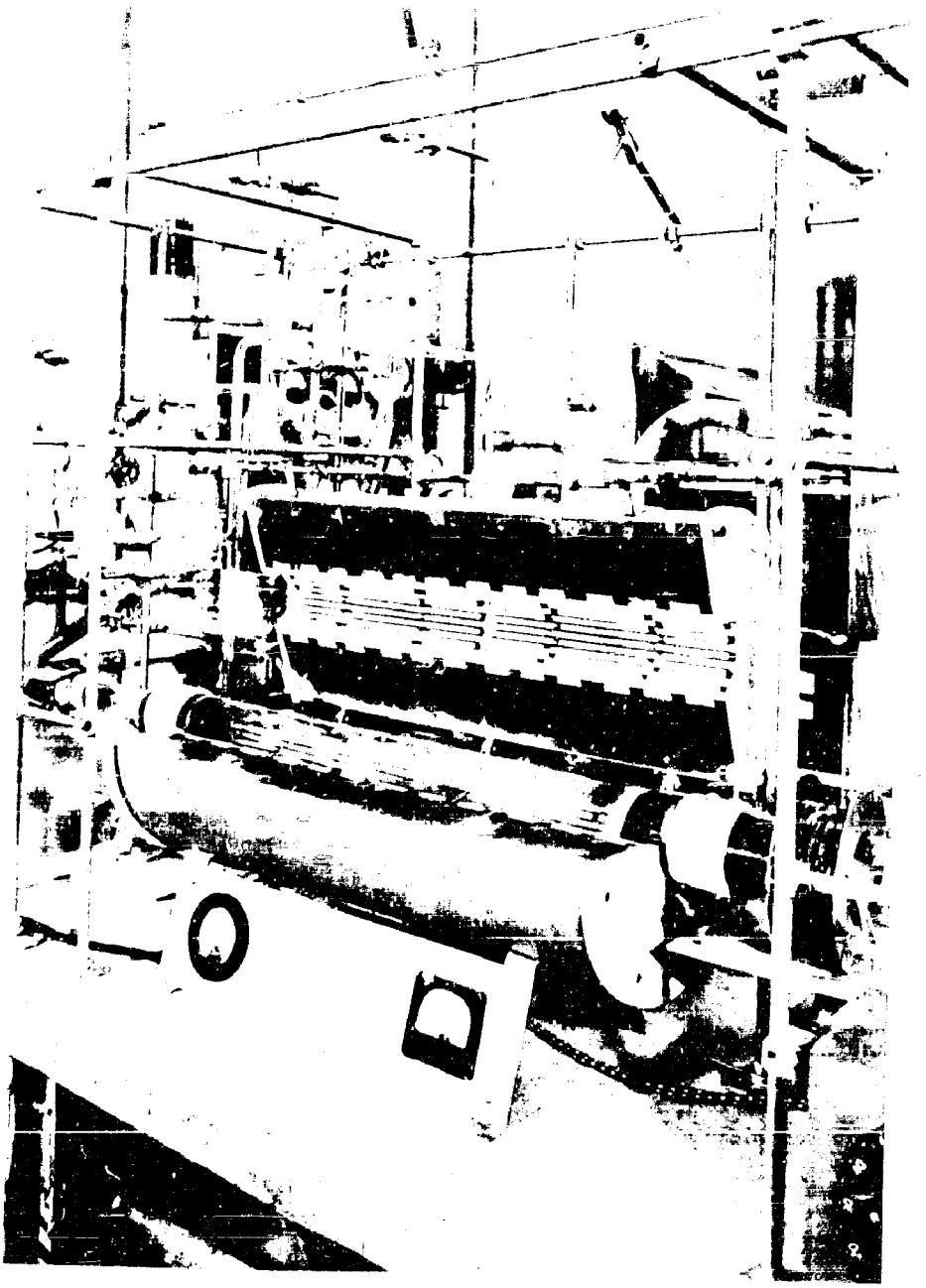


Figure 5
Furnace Opened
To Show Quartz Heating Chamber of Sintering Apparatus

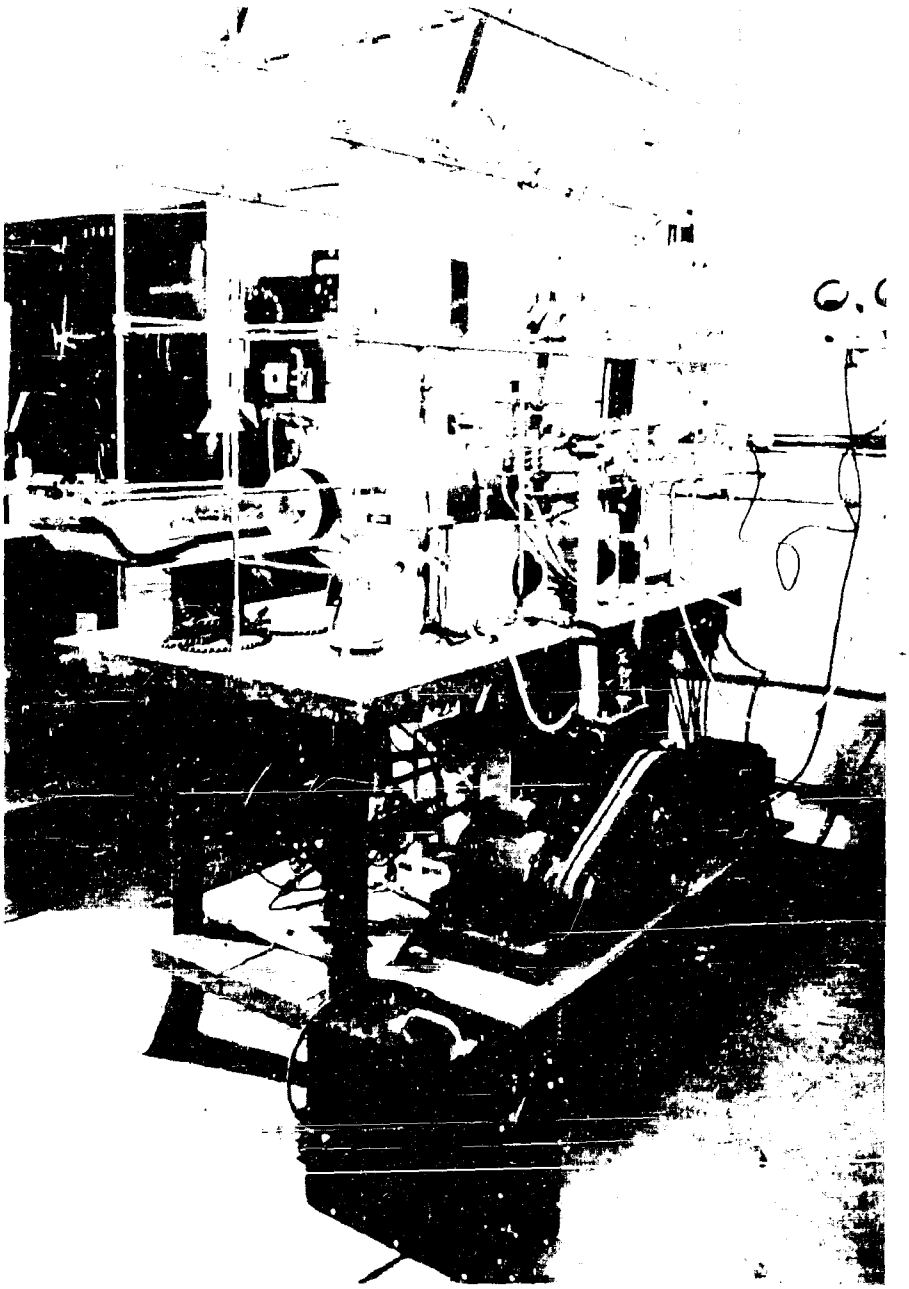


Figure 6

Sintering Apparatus, Showing Vacuum Equipment and Furnace for Purification of Hydrogen

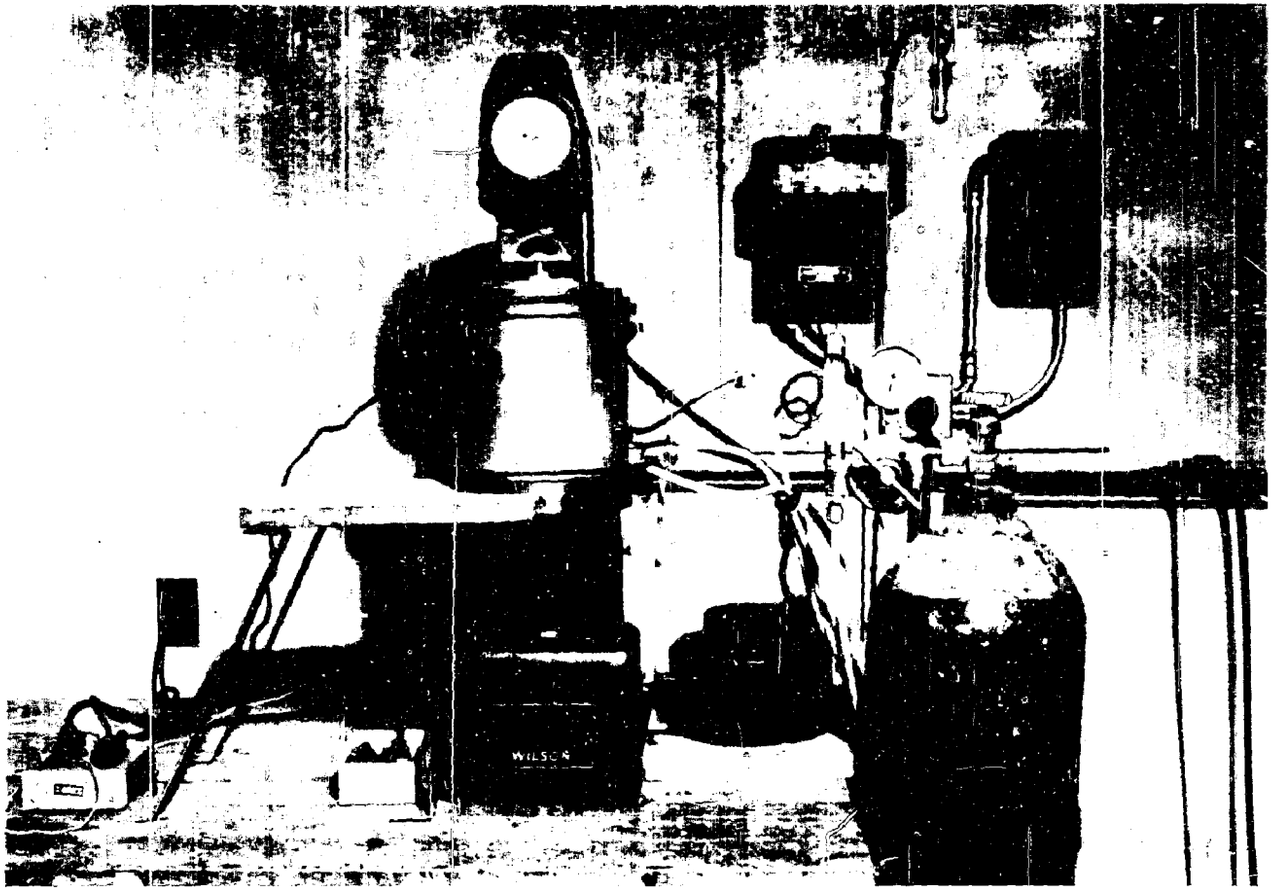


Figure 7a
Hot Hardness Tester in Position

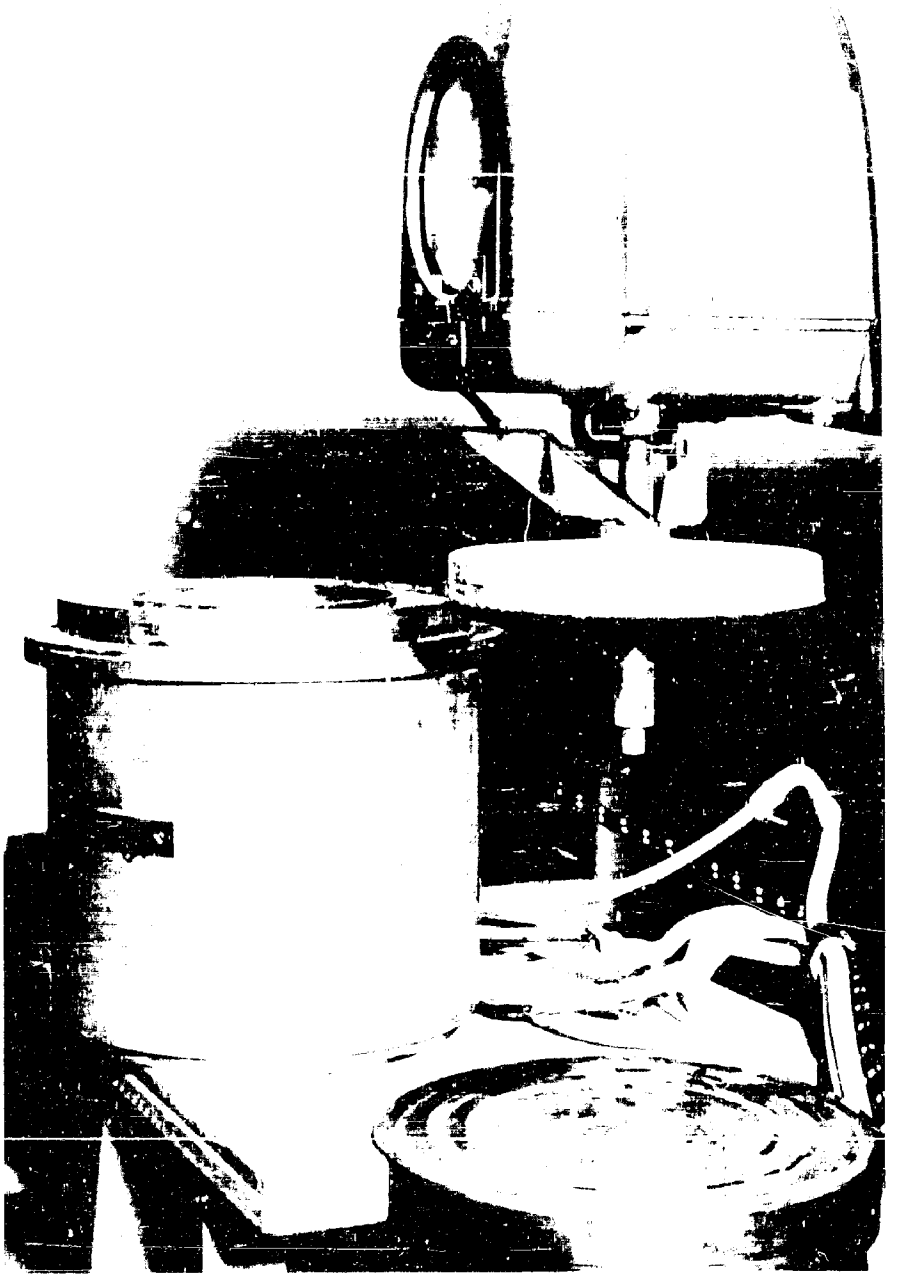


Figure 7b
Detail View of the Indenter and the Spindle

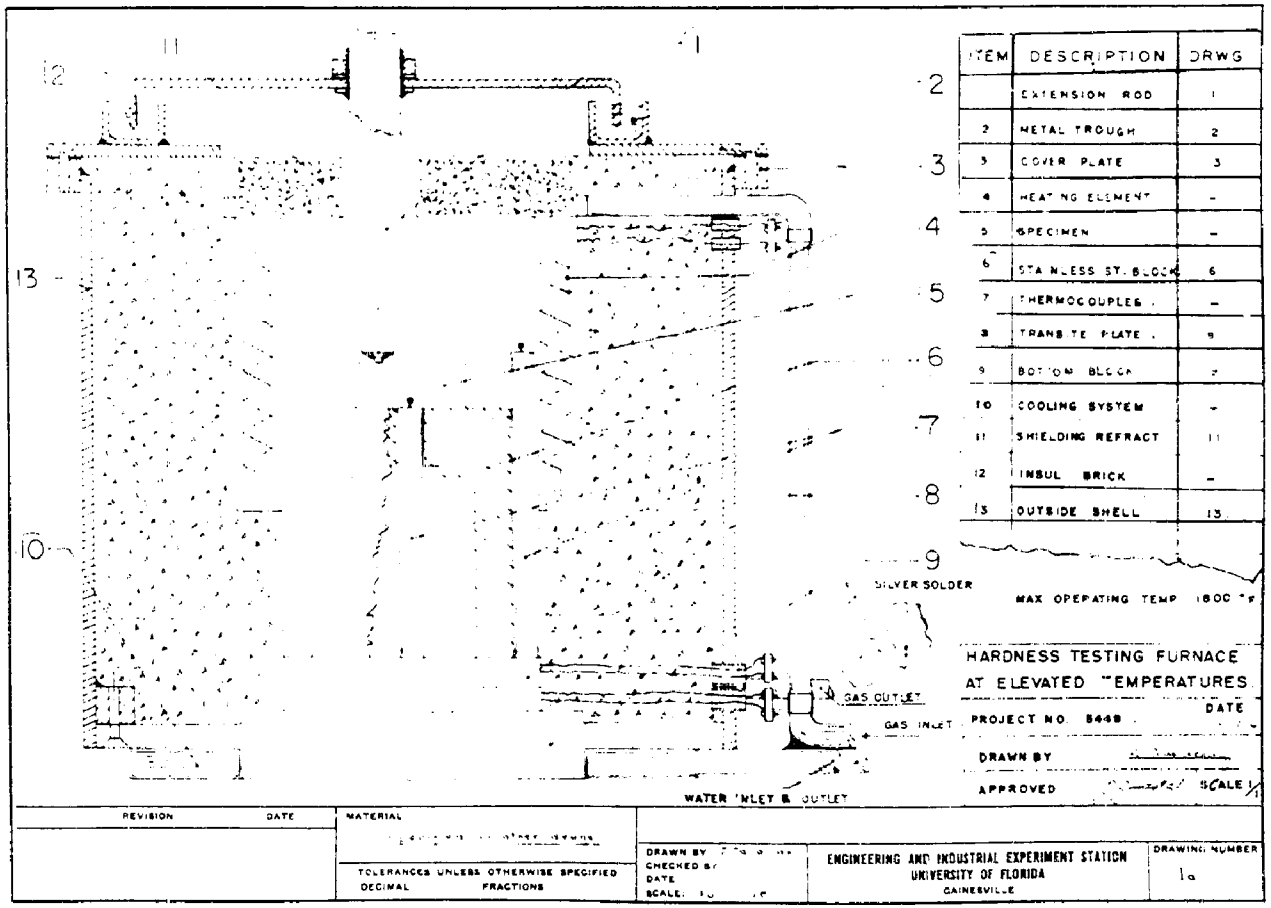

ITEM | DESCRIPTION | DRWG
EXTENSION ROD | 1
2 | METAL TROUGH | 2
3 | COVER PLATE | 3
4 | HEATING ELEMENT | –
5 | SPECIMEN | –
6 | STAINLESS ST. BLOCK | 6
7 | THERMOCOUPLES | –
8 | TRANSITE PLATE | 8
9 | BOTTOM BLOCK | 9
10 | COOLING SYSTEM | –
11 | SHIELDING REFRACT | 11
12 | INSUL BRICK | –
13 | OUTSIDE SHELL | 13
SILVER SOLDER
MAX OPERATING TEMP 1800 °F
GAS OUTLET
GAS INLET
WATER INLET & OUTLET
HARDNESS TESTING FURNACE
AT ELEVATED TEMPERATURES
PROJECT NO. 5448
DATE
DRAWN BY
APPROVED
SCALE
REVISION
DATE
MATERIAL
TOLERANCES UNLESS OTHERWISE SPECIFIED
DECIMAL
FRACTIONS
DRAWN BY
CHECKED BY
DATE
SCALE
ENGINEERING AND INDUSTRIAL EXPERIMENT STATION
UNIVERSITY OF FLORIDA
GAINESVILLE
DRAWING NUMBER
1a

Figure 7c

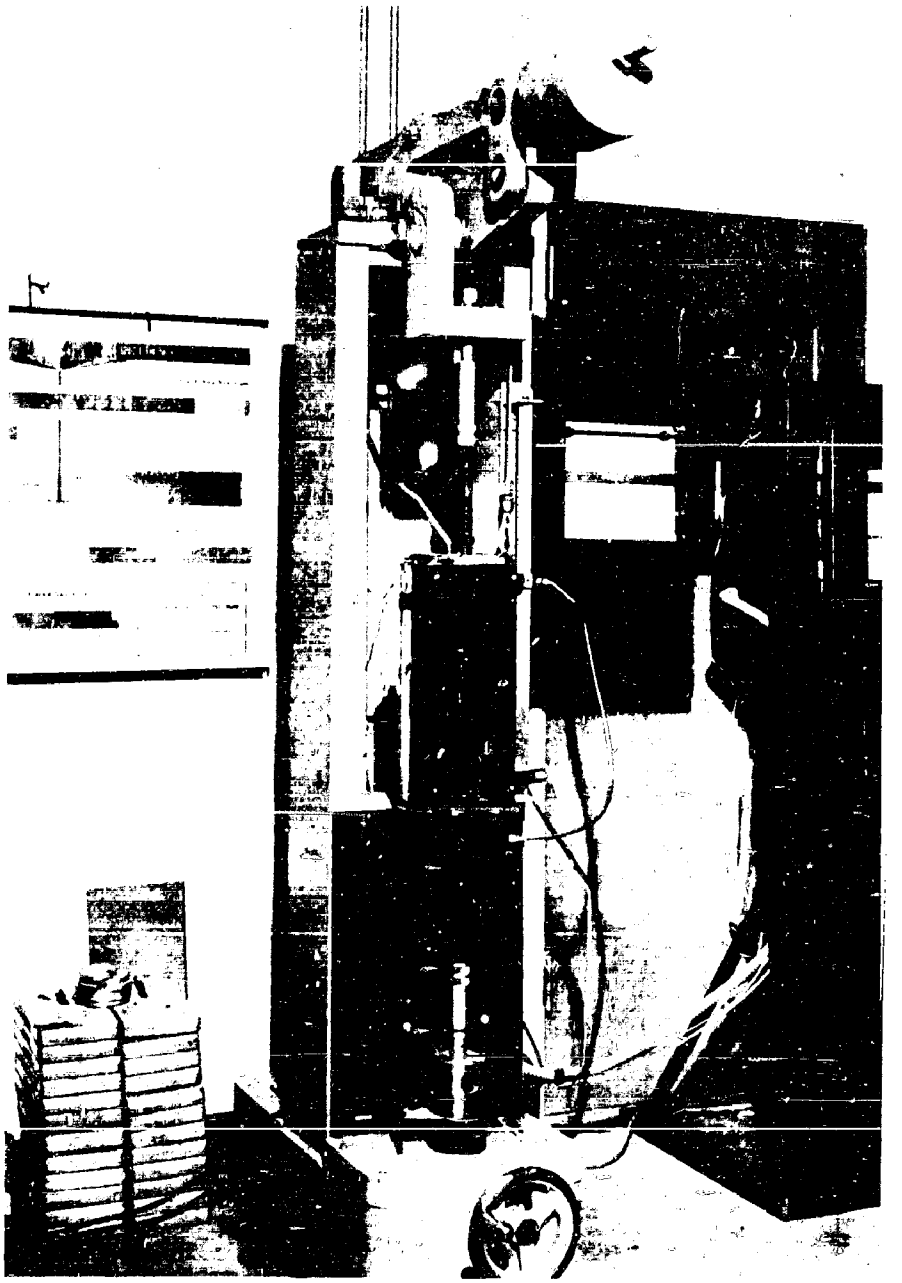


Figure 8a
Creep Testing Unit

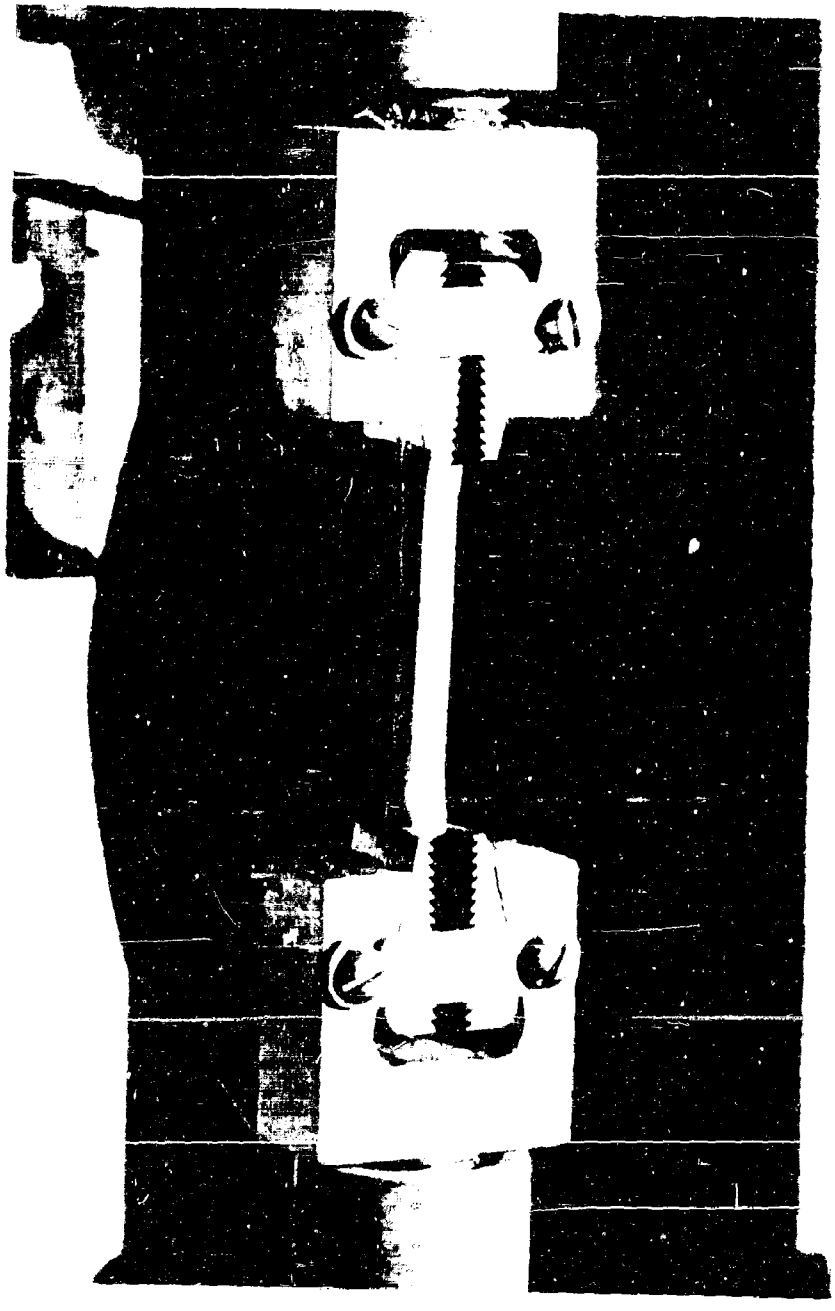


Figure 8b
Tensile Test Bar in Position
to be Tested for Creep Properties

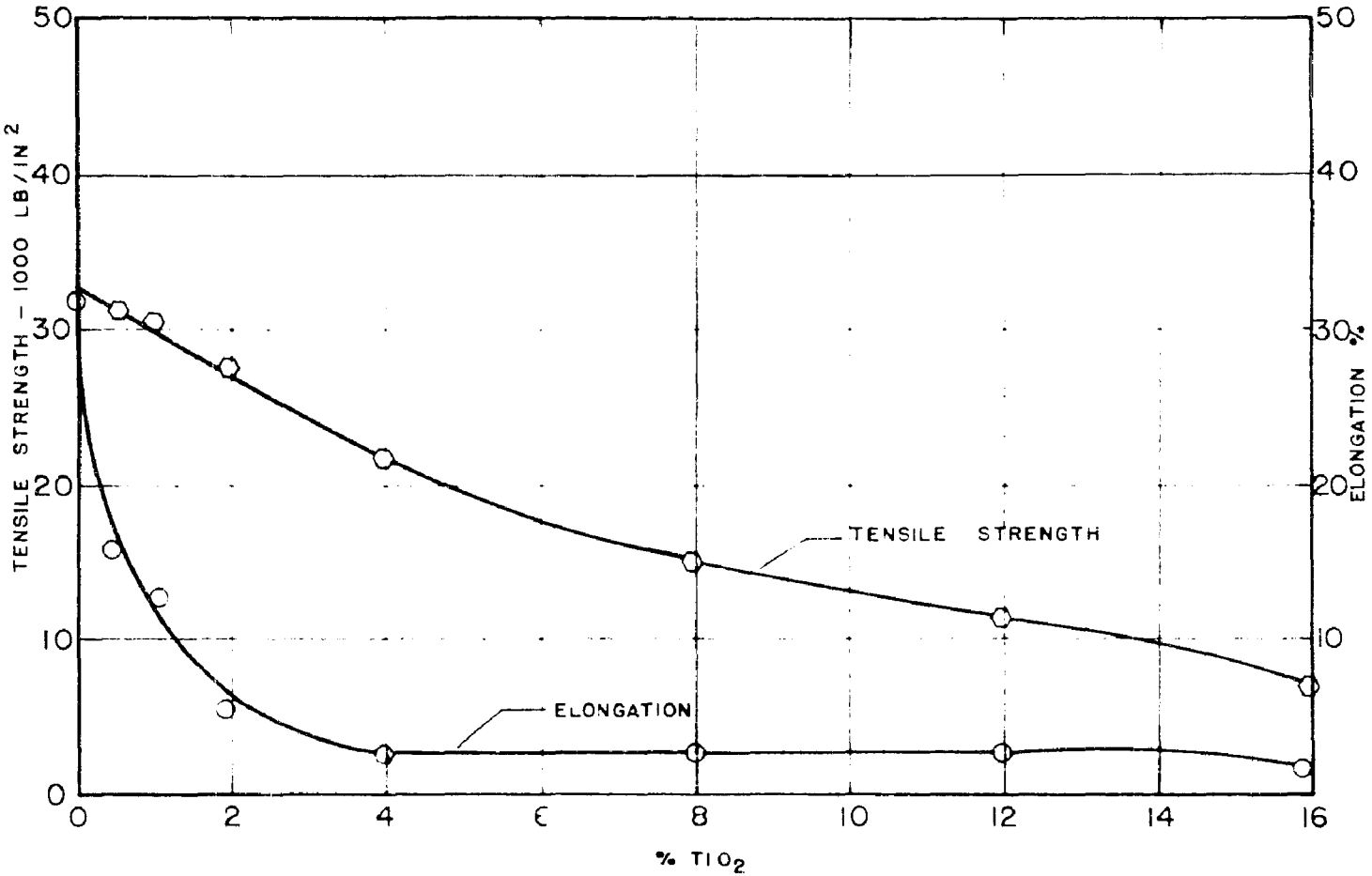


FIGURE 9

THE EFFECT OF TiO_2 ADDITIONS ON THE PROPERTIES OF PRESSED MD 105

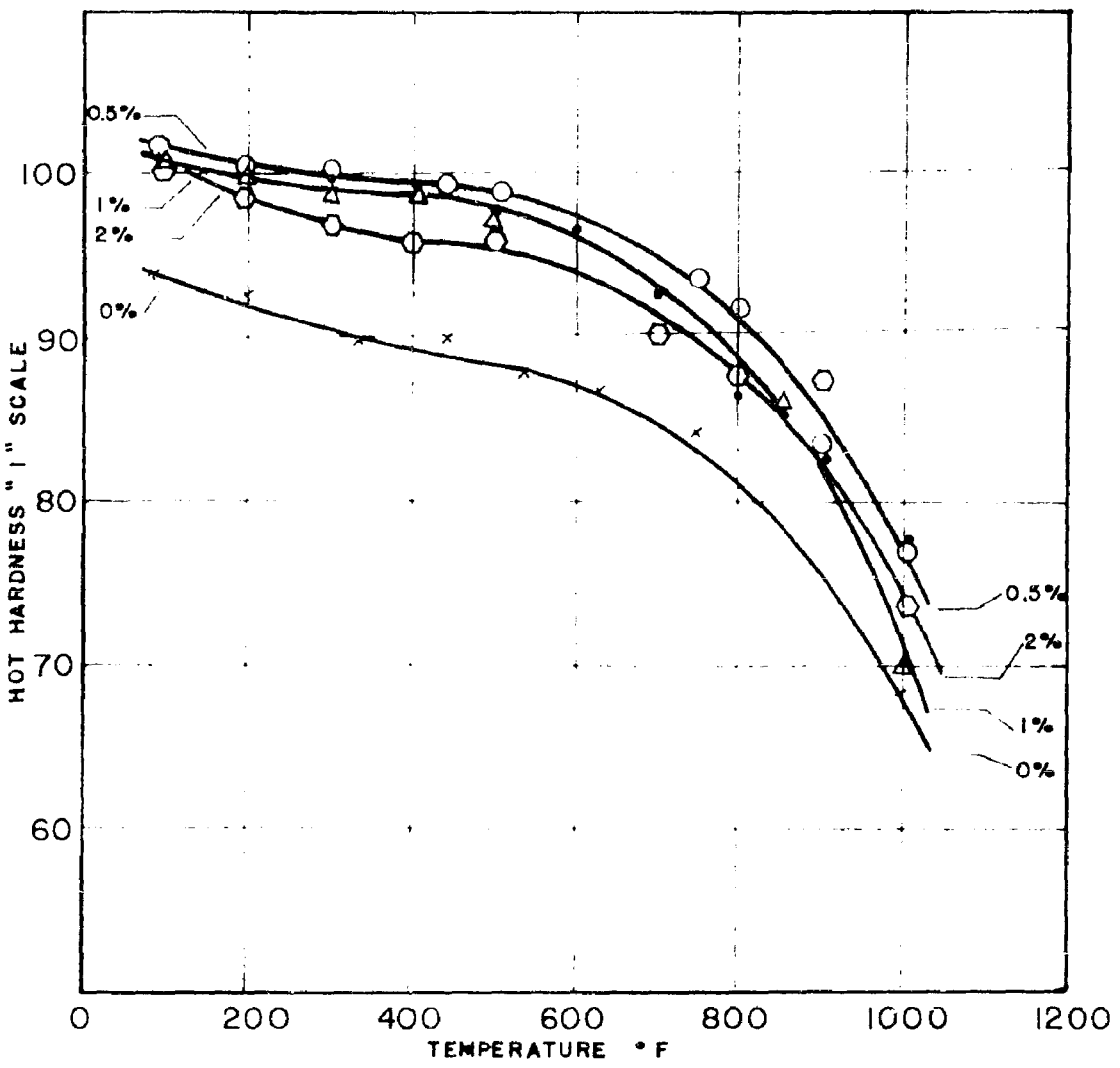


FIGURE 10
EFFECT OF TiO_2 ADDITIONS ON HOT HARDNESS OF MD 105

PART II

TITANIUM POWDERS

INTRODUCTION:

A change was made in the material under study. The effect of titanium dioxide additions to a titanium-tin alloy was determined. Tin has proven to be a useful alloying element in titanium (TML Report No. 19, October 18, 1955) and it was believed that it would bond the titanium powder at temperatures low enough to prevent any reaction of the oxide with the titanium. Tin is soluble in alpha titanium to over 14 atomic per cent (over 25 weight per cent) and is a pronounced alpha stabilizer (M. K. McQuillan, J. Inst. Met., 84 (1955-56)307).

Titanium dioxide should serve as a barrier to grain growth and should impede flow at elevated temperature.

MATERIALS:

The titanium powder was supplied by Metal Hydrides Inc. according to the following specifications:

Chemical Analysis

Ti	95.0	-	98.0% (degassed)
H	0	-	0.3
Ca	0.01	-	0.1
C	0	-	0.1
Fe	0.01	-	0.1
N	0.30	-	0.7
Si	0.01	-	0.2

Screen Analysis

77%	-325	
7	-200	⌿325
7	-200	⌿270
5	-100	⌿200
4	⌿100	

National Formulary grade titanium dioxide (Anatase) was purchased from H. Kohnstamm and Company, Inc. The tin powder was supplied by the McGean Chemical Company according to the following specifications:

Chemical Analysis: Pure virgin Straits tin, 99.8% Sn

Screen Analysis: 94% -325
6 -200 ⌿325

PROCEDURE:

The tin, titanium dioxide and titanium were ball milled for 30 to 45 minutes with enough water to yield a heavy slurry. The balls were separated from the slurry by partially drying the mass over a screen. The resultant material was then pushed through a 20 mesh screen. Agglomerated particles were obtained and were pressed directly. Because of the moisture remaining in the press feed, water was squeezed out of the compact during pressing. This served to displace entrapped air and precluded distortion on sintering.

The die consisted of a 1 1/4 inch diameter plastic molding die shrunk into a mild steel ring of 3 inch wall for reinforcement. (See Figure 2a of Part I of this Report.) In order that the compacted slug could be ejected without cracking, it was necessary to have an 0.008 inch taper on this ejection diameter, load four times up to full pressure, and lubricate the

die walls (Lubriplate). The slugs were sintered either under vacuum or in a helium atmosphere in the apparatus shown in Figure 3 of Part I of this Report. Hot hardness measurements were made on the equipment shown in Figure 7 of Part I of this Report. Density was determined both by the weight-volume method and by weight-in-water, weight-in-air. In this latter method the samples were sprayed with lacquer to seal the pores.

Before hardness readings were made the samples were surface ground for parallel faces. Those specimens tested for hot hardness were further center drilled to admit the thermocouple, as indicated in Figure 7c of Part I of this Report.

Runs were made to evaluate the effects of (a) pressing pressure on hardness and density of sintered compacts, (b) sintering temperature on hardness, (c) sintering time on hardness, (d) tin on hardness and density, and (e) titanium dioxide on hot hardness.

RESULTS:

(a) Effect of Pressing Pressure on Hardness and Density of Sintered Compacts.

Mixes of 8 weight per cent tin, balance titanium, were pressed under pressures varying from 20 to 70 tons per square inch. After vacuum sintering at 1700°F the samples were measured for hardness and density. These data are given in Figures 1 and 2.

(b) Effect of Sintering Temperature on Hardness

The same mix as in (a) was pressed into a sample under 65 tons per square inch. This specimen was sintered at successively higher temperatures from 1100 to 1800°F. The data of this series of runs are presented in Figure 3.

(c) Effect of Sintering Time on Hardness

A sample made as in (b) was sintered at 1700°F over several periods of time, varying from 1/2 hour to 8 hours. The hardness data are shown in Figure 4.

(d) Effect of Tin Content on Hardness and Density

Mixes were made with tin varying from 1 to 20 per cent by weight. They were pressed at 65 tons per square inch and sintered for 2 hours at 1700°F in a helium atmosphere. Hardness and density data are given in Figures 5 and 6.

(d) Effect of Titanium Dioxide Content on Hot Hardness

Mixes were made with tin at 8 weight per cent and varying amounts of titanium dioxide (0 to 16 weight per cent), pressed at 65 tons per square inch, and sintered for 2 hours in a helium atmosphere at 1700°F. The compacts were tested for hot hardness (under a helium atmosphere) and the data are given in Figure 7. Also plotted on the same graph are the data taken on a wrought alloy containing 6 per cent aluminum, 3 per cent molybdenum, and a qualitative indication of boron. This alloy was supplied by Dr. F. A. Crossley of the Armour Research Foundation.

DISCUSSION:

Hardness and density increased with pressing pressure, but 65 tons per square inch was chosen as the pressing pressure to use in the following experiments because of die wear and distortion at the higher pressures. Hardness also increased with temperatures, but 1700°F was selected as the sintering temperature because of the limitations of the sintering chamber. After a rapid rise in hardness during the first sintering periods the specimen did not change appreciably in hardness from 2 to 8 hours and the former was selected as the sintering time.

Tin content did not change the hardness significantly but it did increase the density markedly. It should be noted that the densities of the compacts were about 80 per cent of theoretical. The value of 8 per cent tin was selected since it did not raise the density too much and yielded good bonding of the titanium.

As expected, the presence of titanium dioxide in the specimen resulted in improved hot hardness, but the best values were below the performance of the wrought alloy. A 12 per cent addition of titanium dioxide to the 8 per cent tin base had the highest hot hardness values over the range tested (100-1200°F). The addition of titanium dioxide did not lower the density. This can be explained by considering that the oxide served to fill the pores of the compact. There is some potential to these alloys as new light weight engineering materials.

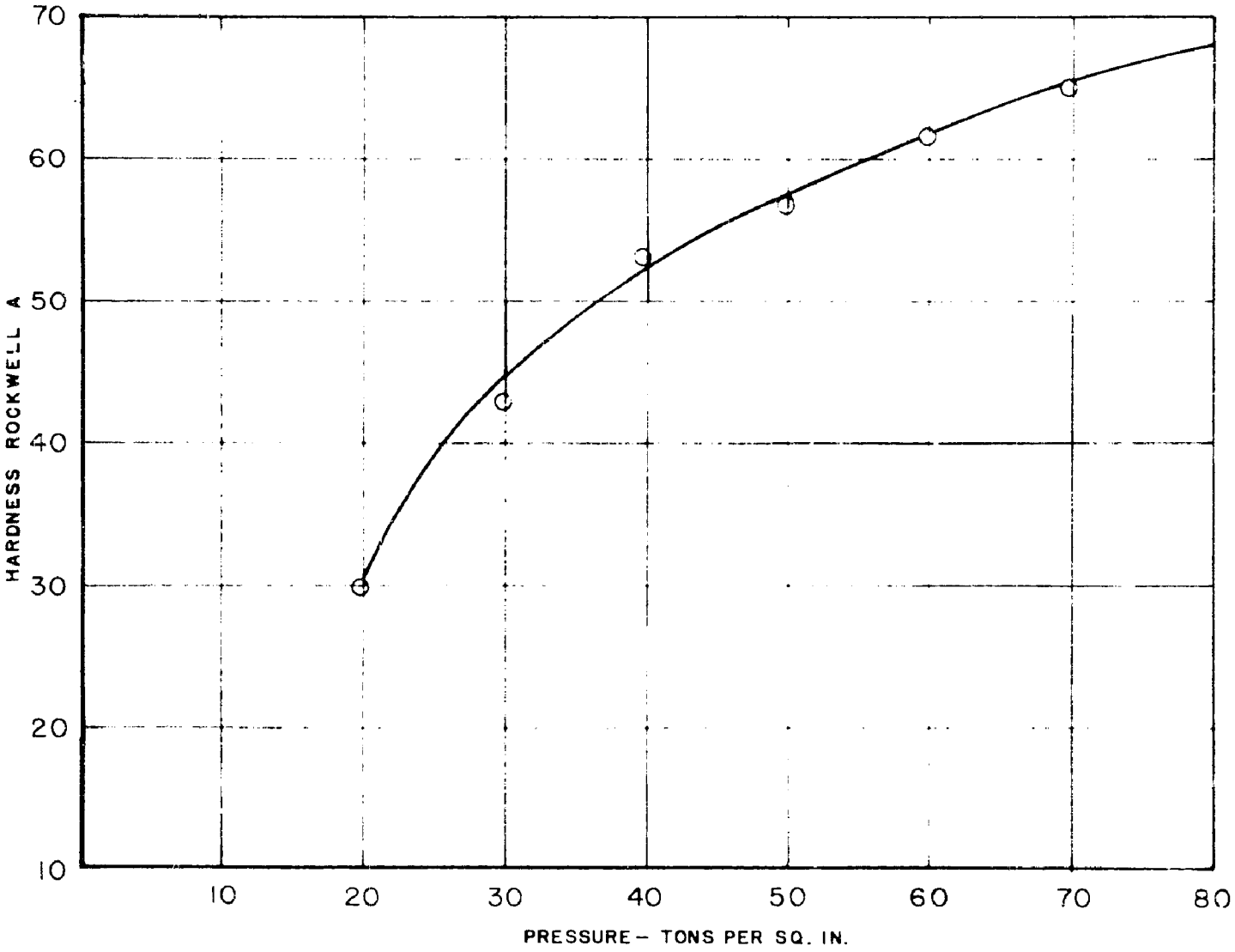


FIGURE 1
EFFECT OF PRESSING PRESSURE ON HARDNESS

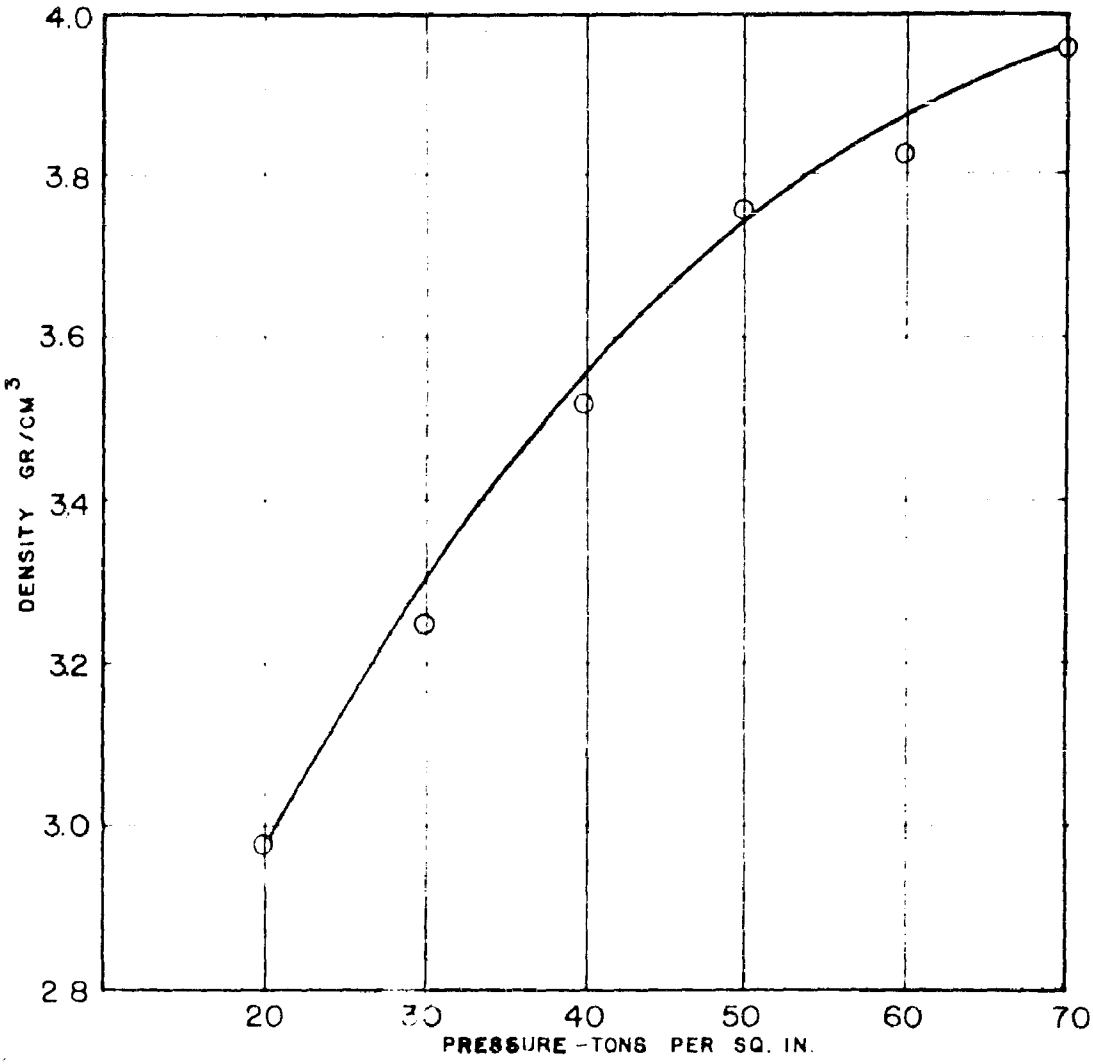


FIGURE 2
EFFECT OF PRESSURE ON DENSITY

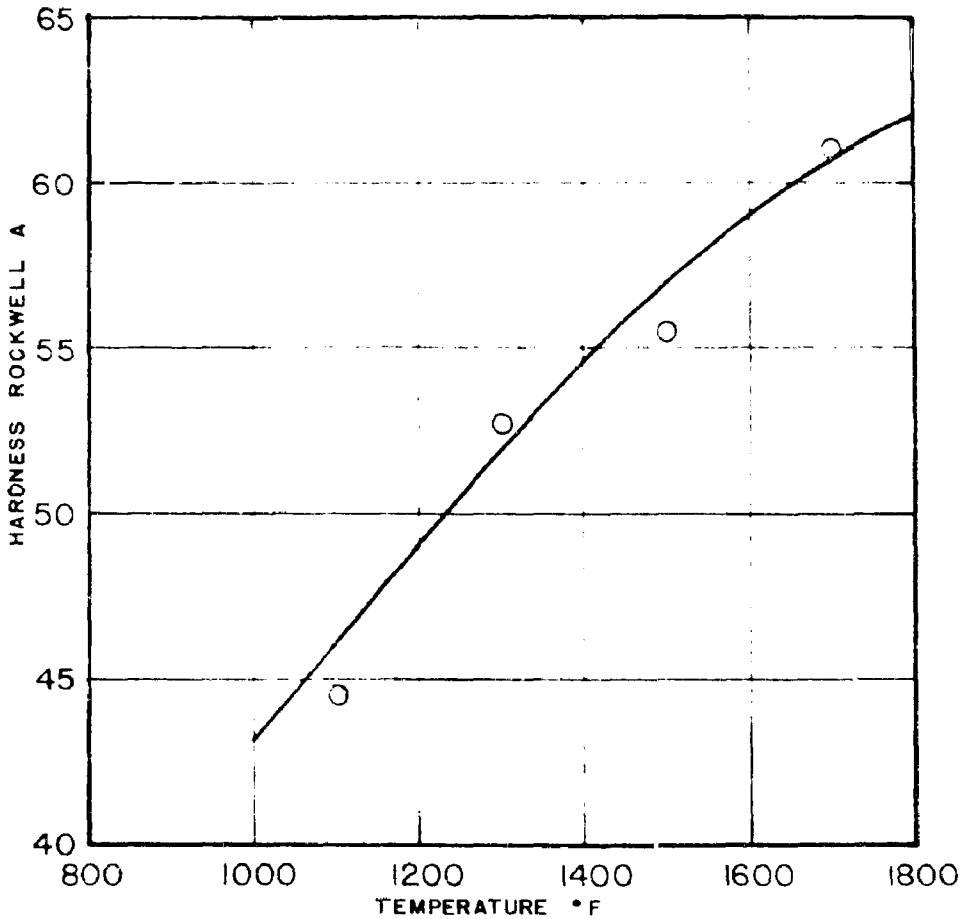


FIGURE 3
EFFECT OF SINTERING TEMPERATURE ON HARDNESS

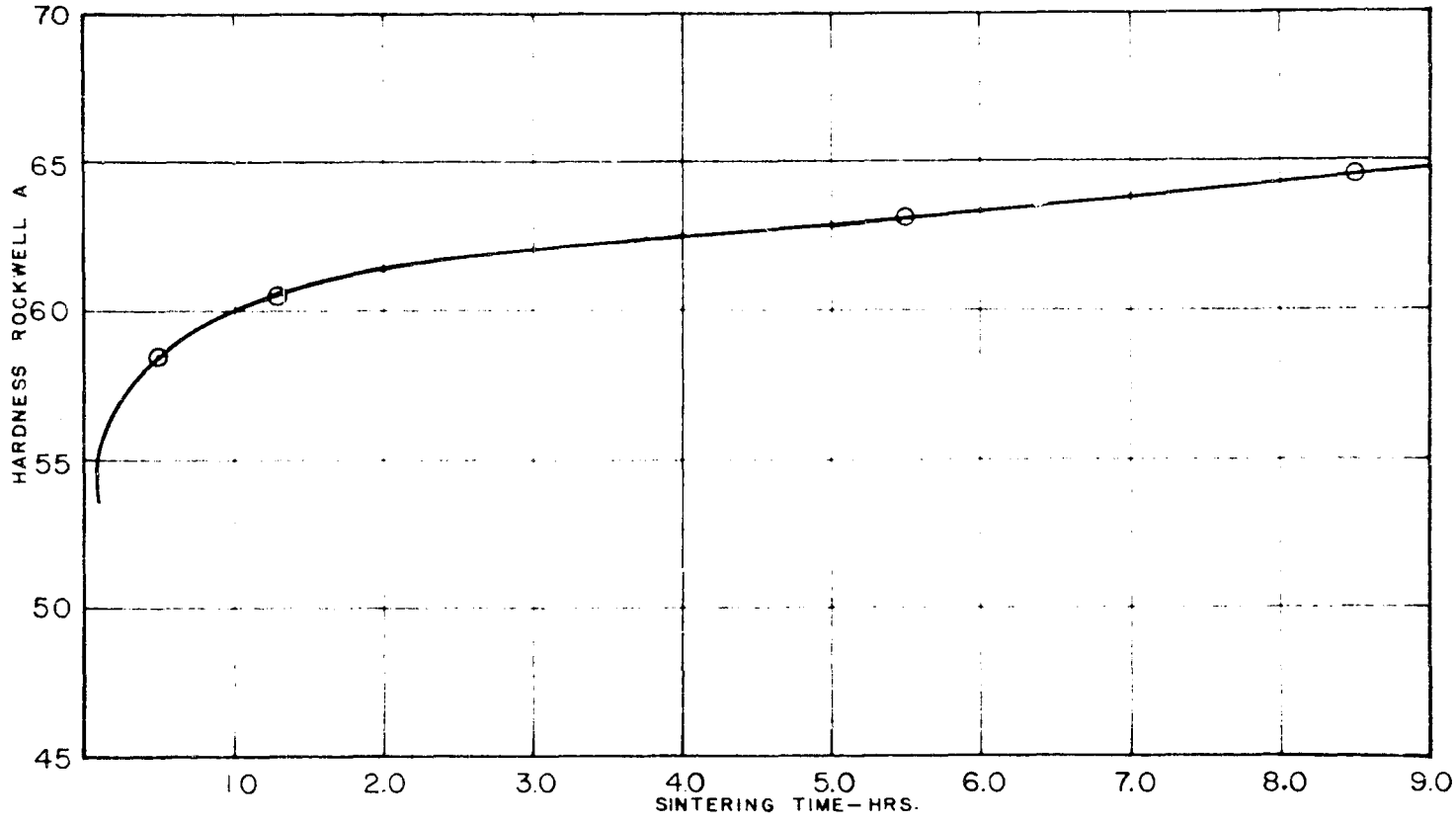


FIGURE 4

EFFECT OF SINTERING TIME ON HARDNESS

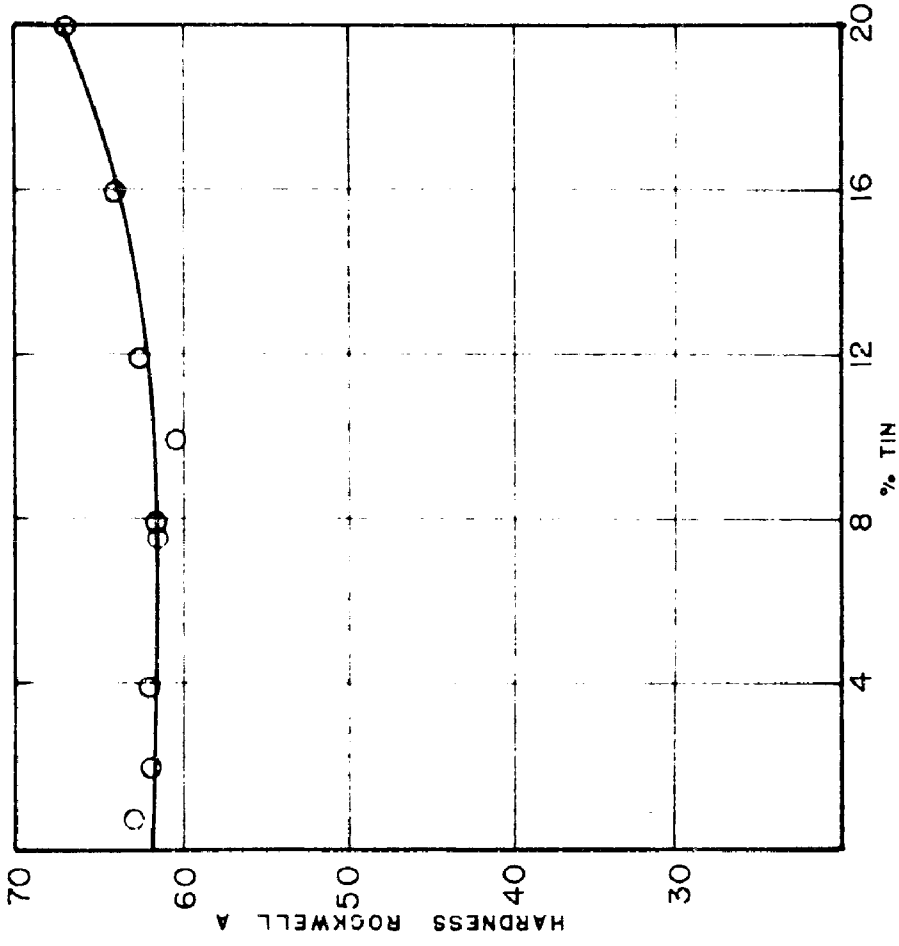


FIGURE 5
EFFECT OF TIN ON HARDNESS

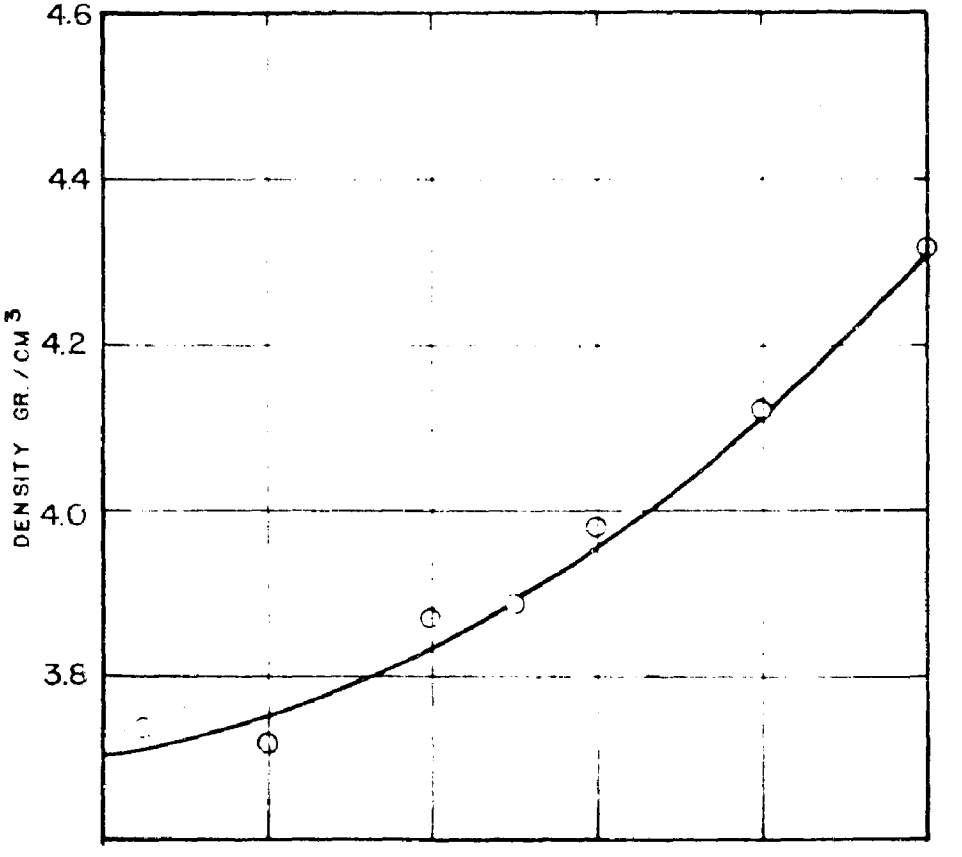


FIGURE 6
EFFECT OF TIN ON DENSITY

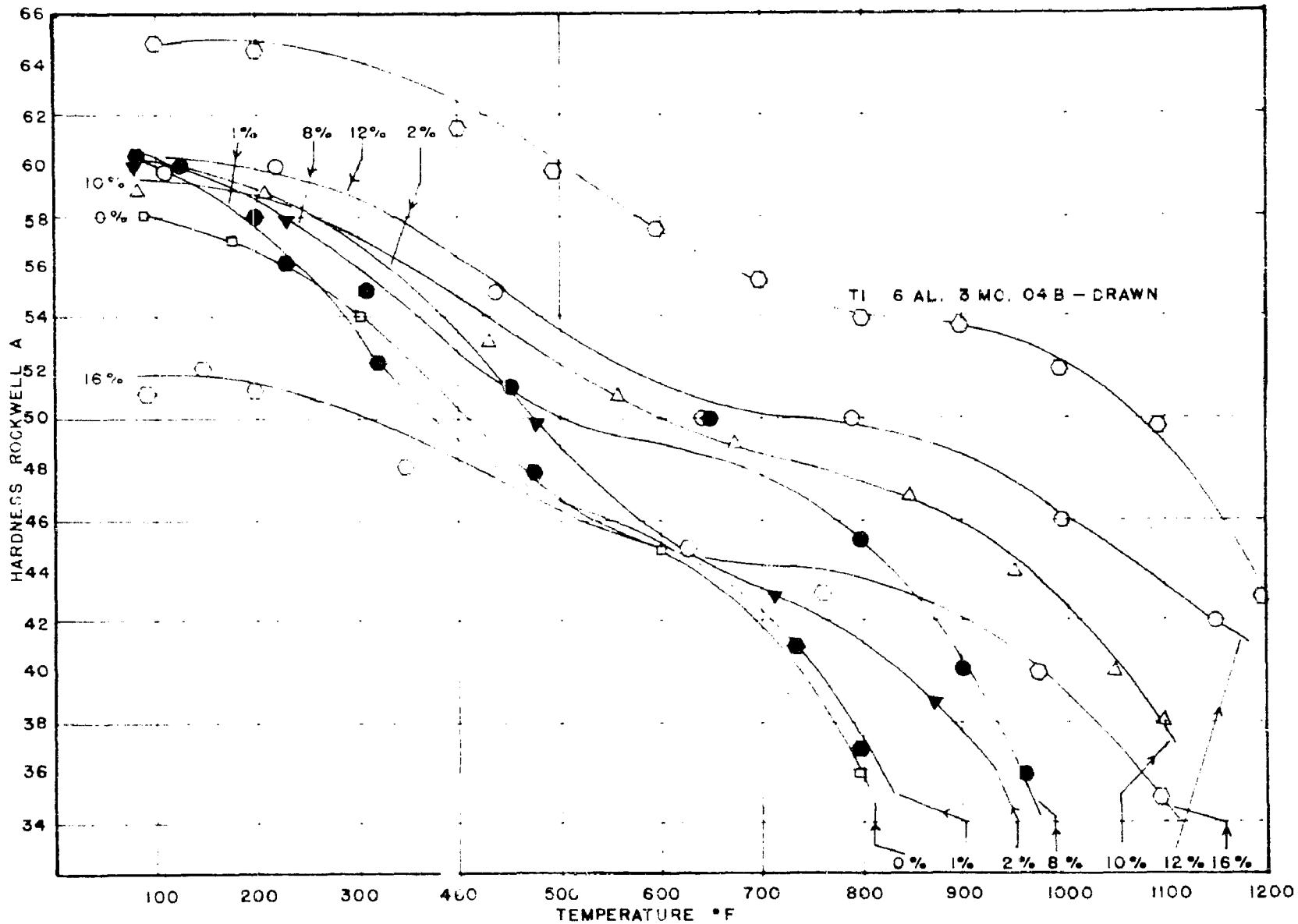


FIGURE 7

EFFECT OF TITANIUM DIOXIDE ON THE HOT HARDNESS OF ALLOY

PART III

ZIRCONIUM POWDERS

INTRODUCTION:

The work of this phase was confined to the study of zirconium alloys made from mixtures of the metal powders and zirconium hydride. The major emphasis was placed on zirconium-tin alloys. Due to the presence of impurities, probably nitrogen and oxygen, the compacts were brittle and hard. These materials had excellent corrosion resistance to acids but did not have the same order of corrosion resistance that pure crystal bar zirconium has. Zirconium hydride was chosen as the starting material because of the excellent results reported by H. H. Hausner and H. S. Kalish (see "Metallurgy of Zirconium," B. Lustman and F. Kerze, Jr., McGraw-Hill Book Co., 1955, pp. 280-302). They achieved theoretical density of 6.59 grams per cubic centimeter at 50 tons per square inch pressure followed by a sintering treatment at 1200°C for 5 hours under a vacuum of 2×10^{-5} mm Hg at temperature. Upon being heated above 400°C in a vacuum the hydride begins to decompose and hydrogen is evolved, leaving highly active surfaces on the zirconium particles, which should serve to promote rapid sintering.

MATERIALS:

The zirconium hydride powder was purchased from Metal Hydrides, Inc., as Grade E powder, and analyzed 96.9 per cent zirconium and 1.98 per cent hydrogen, with an average particle size of 4.1 microns. It was principally epsilon ZrH. The tin powder was purchased from the McGean Chemical Company as pure

virgin Straits tin, containing 99.8 per cent tin (beta-phase) with 94 per cent of the powder through 325 mesh and the balance through 200 mesh. Carbonyl iron powder, Grade L, (99.6 - 99.9 per cent iron, average particle diameter of 20 microns) was supplied by Antara Chemicals Division of General Dyestuff Corporation, and 99.9 per cent nickel powder (100 mesh) was obtained from the Oak Ridge National Laboratory. Acheson graphite powder, grade GP 38, was purchased from the National Carbon Company. The silver was purchased from Goldsmith Bros. as 100 mesh, high purity powder.

The addition agents described above were selected as materials which would alloy with zirconium and possibly overcome the deleterious effects of oxygen and nitrogen as well as promote sintering. It was expected that tin would permit good bonding when non-metallic aggregates were added, since it would be liquid for part of the time during sintering and should flow around the particles. Graphite was studied as a non-metallic addition that should provide lubrication during pressing as well as act as a barrier to grain growth. It was expected that the carbide which formed during sintering would act as a further impediment to grain growth of the zirconium.

PROCEDURE:

The powders were, at the beginning of this study, blended with xylene. It was thought that the xylene would improve the mixing and prevent air from being entrapped in the compact during pressing. A presintering operation was required to

volatilize the xylene; this consisted of heating for 1 hour at 425 to 525°C under a slight positive pressure of hydrogen.

It was found that the milling operation with xylene was not necessary, and standard procedure consisted of the following steps:

1. mix powders dry in jar mill, with pebbles,
2. press at 65 tons per square inch,
3. sinter at 950°C in vacuum.

Zirconium hydride had a tendency to seize to the hardened steel walls of the die and galled upon ejection. It was found necessary to lubricate the walls of the die with a dry molybdenum disulfide lubricant (Molykote powder) to avoid scoring of the die walls and to avoid cracking of the compacts upon ejection.

When xylene was used, some reaction occurred between it and the hydride during presintering to yield a very unpleasant smelling product.

X-ray diffraction patterns were made to determine the crystalline forms of the components present in the compacts.

The compacts were pressed in the die and sintered in the vacuum furnace described in Part I of the Report. Tensile bar specimens could not be pressed because of the seizure between the hydride and the die walls. The chatter during ejection completely shattered the green tensile bar. The ratio of the area in contact with the die walls to the total area of the compact was about twice as great in the tensile specimen as it was in the cylindrical specimen.

Microscopic examination did not yield any observations of value other than disclosing the presence of a very finely dispersed precipitate throughout the material. The specimens could not be prepared by the chemical polishing procedure useful on crystal bar zirconium and on Zircaloy-2 because of their lowered corrosion resistance. Even diamond polishing did not prepare the surface well enough to show the extinctions usually observed when zirconium is rotated in polarized light.

During sintering the compacts were supported on trays. At first the trays were of stainless steel, floored with zirconium sheet; but because of reaction between the two metals and the tin of some of the compacts, a graphite cylinder was used as the boat for the balance of the sinterings.

Hot hardness determinations were made by use of the apparatus described in Part I of this Report. A helium atmosphere prevented excessive oxidation.

RESULTS:

The effect of pressing pressure was determined on a 16 per cent tin -5 per cent graphite mix, using a 24 hour sinter at 810°C (Figure 1). A pressure over 50 tons p.s.i. was found to be necessary to obtain compacts of good bond strength. The compact pressed at 35 tons p.s.i. was so loosely bonded after the sinter that upon grinding it emitted an intense, white spark stream with almost explosive violence. The sintered specimens consisted of zirconium, tin, graphite, zirconium carbide, and undecomposed zirconium hydride.

A series of specimens with a 5 per cent graphite base and various tin contents up to 8 per cent were pressed and sintered for 132 hours at 870°C (Figure 2). All the hydride had decomposed but considerable amounts of zirconium carbide had formed; excess graphite was also present.

A series of specimens with 8 per cent tin base and various graphite contents up to 6 per cent were pressed and sintered for 35 hours at 950°C (Figure 3). Increased carbon resulted in decreased density and markedly decreased hardness. The amount of carbide formed increased with the graphite content.

Two series of specimens were made in which tin was varied up to 24 per cent, balance zirconium. The first series (Figure 4) was milled with xylene, as were all the mixes described previously. The second series (Figure 5) was milled dry, as were all mixes to be subsequently described. No benefits of xylene milling were found and the practice was abandoned. Surprisingly, tin additions above 4 per cent decreased the density and the hardness of the sintered compacts. The compacts also lost much of their corrosion resistance. Additions up to 4 per cent tin increased the density and the hardness upon 60 hours sintering at 950°C. The hardness increased up to 8 per cent tin in the series sintered for only 6 hours at 950°C.

Although these specimens were sintered on zirconium strip supported by stainless steel trays, they had dull gray surfaces upon removal from the sintering furnace. X-ray diffraction analysis showed this coating to be zirconium carbide. After removal of this coating by grinding and after etching in

50 ml nitric acid-50 ml water containing a few drops of hydrofluoric acid for 15-30 minutes, a well-defined X-ray diffraction pattern of hexagonal alpha-zirconium was obtained (see Table and Figure 6). The specimen was hard (42 Rockwell C) and unmachinable.

The effect of tin on the X-ray diffraction pattern was negligible until the composition corresponding to Zr_4Sn (24% Sn) was reached; even then, the pattern of alpha Zr was dominant. This indicated that tin may have been lost by volatilization during vacuum sintering. X-ray data for the specimens of Figure 5 are given in the Table.

The iron zirconium alloys, on the other hand, developed extra lines, probably due to Fe_2Zr, at 1 per cent iron addition. Iron also increased the sintered density and the sintered hardness (Figure 7).

Nickel did not produce as high a sintered density as did iron even though, of itself, it is a denser metal. The hardness decreased with increased nickel content (Figure 8). The X-ray diffraction pattern disclosed the presence of a second phase, presumably Zr_2Ni, in the 1 per cent nickel and higher alloys.

The addition of silver up to 4 per cent increased the density and decreased the hardness (Figure 9). This effect on the density was in contrast to the effect of tin, which, as noted previously, produced a decrease in density beyond a 1 per cent addition.

Hot hardness determinations were made on several specimens containing tin (for which the hardness and density data are

presented in curves B of Figure 5). The results are shown in Figure 10. The drop in hardness with temperature of these specimens closely paralleled the drop for Zircaloy-2; but the hardness values were all higher since the material was so much harder at room temperature. The high purity iodide zirconium dropped off in hardness with temperature very rapidly.

DISCUSSION:

The compacts produced in this study were much harder than the sintered materials reported in the literature. The hardness of dense sintered zirconium is reported as 90 to 94 Rockwell B (Metallurgy of Zirconium, p. 296). It is also reported to have high ductility and to be readily cold rolled. The dense zirconium produced had a hardness of 40-45 Rockwell C. This was undoubtedly due to oxygen and nitrogen; it is believed that this contamination may have taken place during sintering even though a vacuum 5×10^{-4} mm Hg was achieved at 950°C after the hydrogen had been expelled. The hydride powder, itself, may have contained sufficient oxygen and nitrogen to result in the hard and brittle sintered material produced. Some molybdenum sulfide was picked up by the compact due to its being used as a die lubricant, which could also have added to the hardness.

Alloy additions served to raise the hot hardness, but the most marked hardening agents were the contaminants, oxygen and nitrogen.

HIGH PURITY ZIRCONIUM:

Another attempt (see Status Report 5) was made to prepare compacts of zirconium for grain growth study. A special grade of high purity zirconium hydride was purchased from the Metal Hydrides, Inc., ($35.00 per pound).

The procedure for preparation of specimens was similar to that described previously, except that the sintering was carried out in a smaller apparatus capable of reaching higher vacuums than the equipment used for the iron specimens.

Compacts of the pure hydride were made by pressing in the carbide pellet press without using any lubricant. They were pressed at 35 tons per square inch and sintered for one-half hour at 950°C under vacuum. The sinterings were then repressed at 75 tsi and resintered under vacuum for times varying from one-half hour to two hours.

Despite the fact that very fine zirconium hydride was used, and that the hydrogen had been brought down to an equilibrium pressure of 10^{-5} mm at 950°C, the sinterings were heavily cracked and very little densification had occurred.

TABLE

X-ray Diffraction Data on Sintered Specimens of Zirconium-Tin Alloys

	d values							
Crystal Bar Zirconium	0% Sn	0.5% Sn	1% Sn	2% Sn	4% Sn	8% Sn	16% Sn	24% Sn weak reflections
Sintered 6 hours at 950°C								
2.798	2.805	2.805	2.805	2.804	2.804	2.804	2.804	
2.573	2.586	2.580	2.586	2.585	2.585	2.585	2.585	
2.459	2.469	2.465	2.469	2.469	2.469	2.469	2.469	
1.894	1.899	1.899	1.899	1.899	1.899	1.899	1.899	
1.616	1.618	1.618	1.618	1.618	1.615	1.615	1.618	
1.463	1.467	1.467	1.467	1.467				
1.397		1.400	1.402	1.406				
1.368	1.372	1.372	1.372	1.372				
1.350	1.354	1.354	1.354	1.353				
			- - - OTHER LINES - - -					
							2.89	
							2.76	
				2.68			2.68	
				2.49			2.49	
						2.39	2.38	
Sintered 60 hours at 950°C								
	2.80	2.804	2.804	2.796	2.796	2.796	2.796	2.796
	2.58	2.578	2.580	2.578	2.586	2.578	2.586	2.586
	2.469	2.469	2.469	2.462	2.462	2.462	2.462	2.462
	1.90	1.899	1.899	1.895	1.899	1.895	1.895	1.899
	1.62	1.618	1.617	1.615	1.615	1.613	1.615	1.613
	1.467	1.467	1.467	1.465	1.465	1.467	1.467	1.465
		1.400	1.402		1.400			
	1.373	1.372	1.372	1.370	1.370	1.368	1.372	1.368
	1.354	1.353	1.353	1.351	1.351	1.349		1.349
			- - - OTHER LINES - - -					
							2.90	2.90
					2.76	2.76	2.76	2.76
						2.49	2.49	2.49
							2.388	2.392

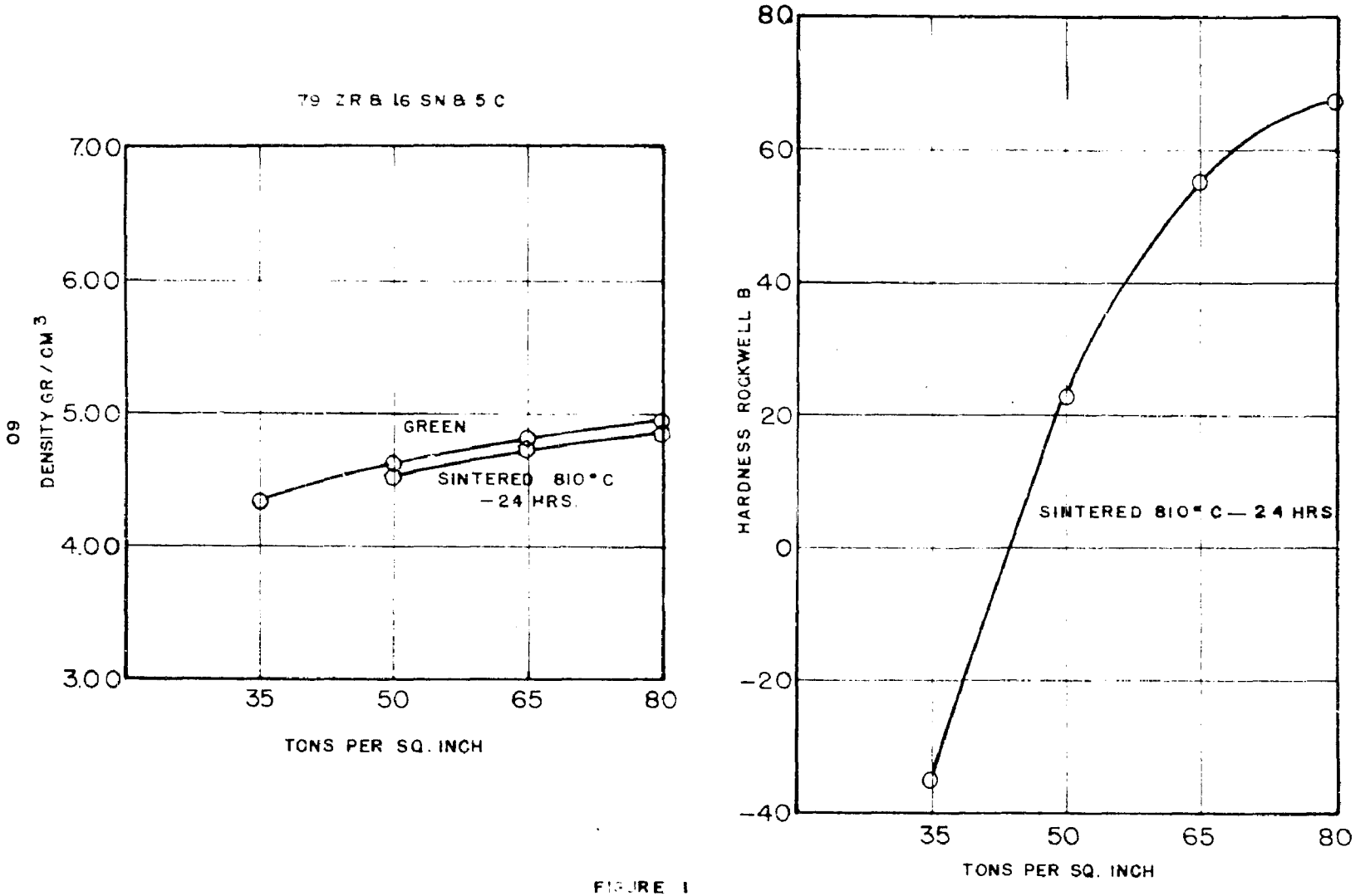


FIGURE 1
EFFECT OF PRESSING PRESSURE (XYLENE MIX)

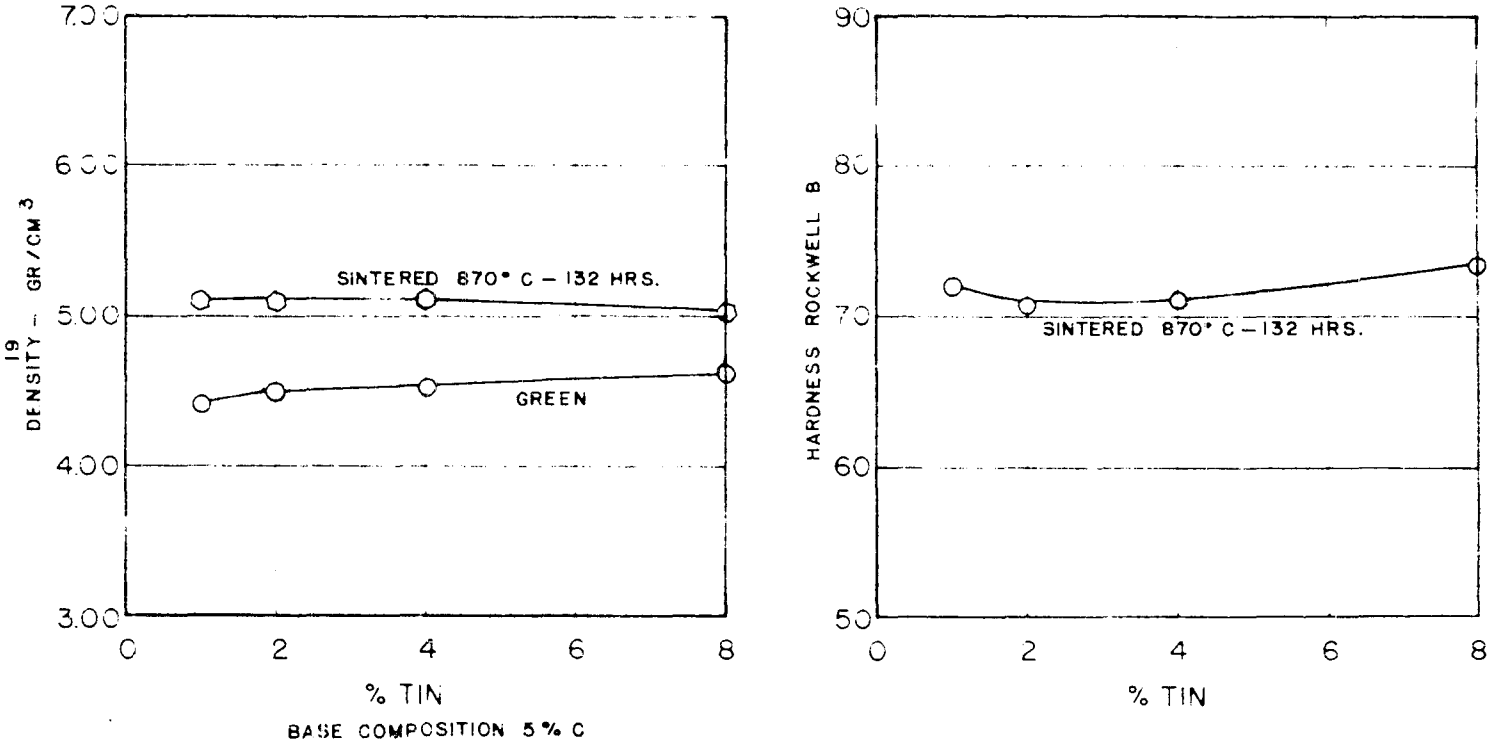
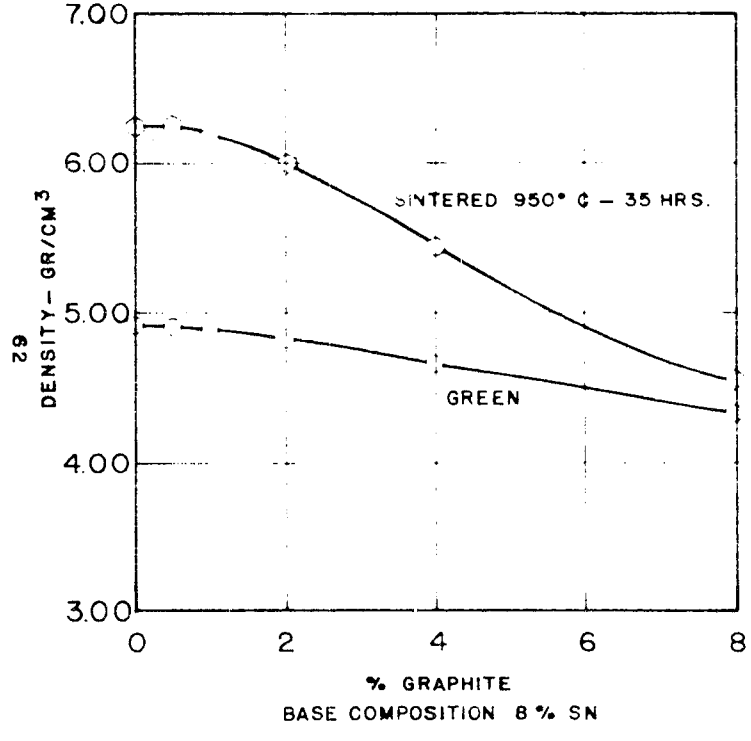


FIGURE 2
EFFECT OF TIN ON ZIRCONIUM – 5% GRAPHITE ALLOYS (XYLENE MIX)



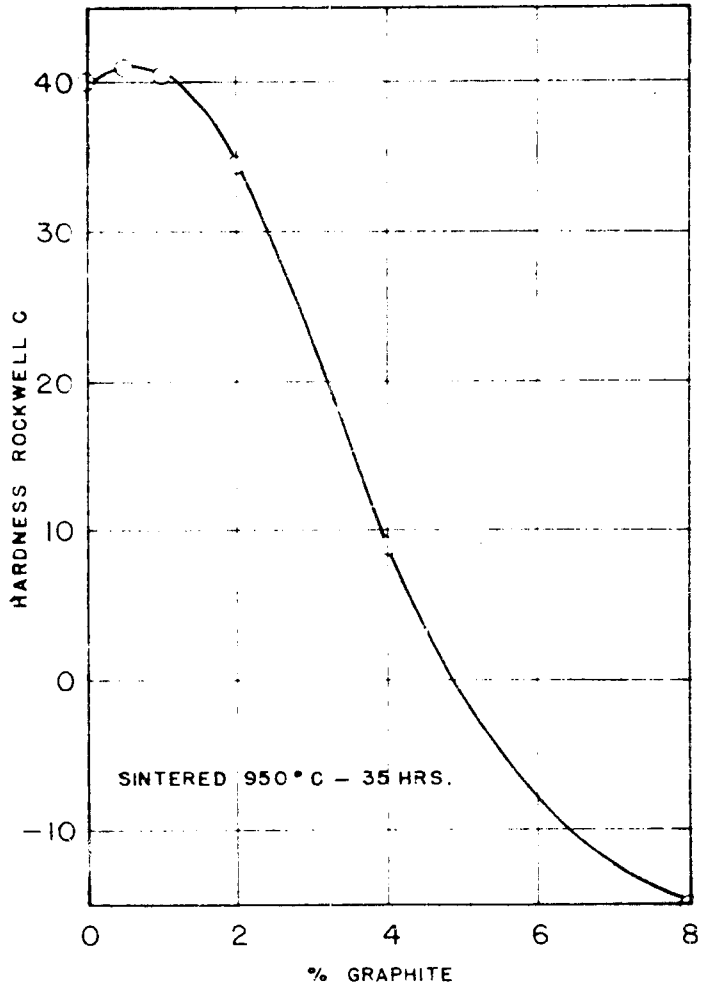


FIGURE 3
EFFECT OF GRAPHITE ON ZIRCONIUM - 8% TIN ALLOYS (XYLENE MIX)

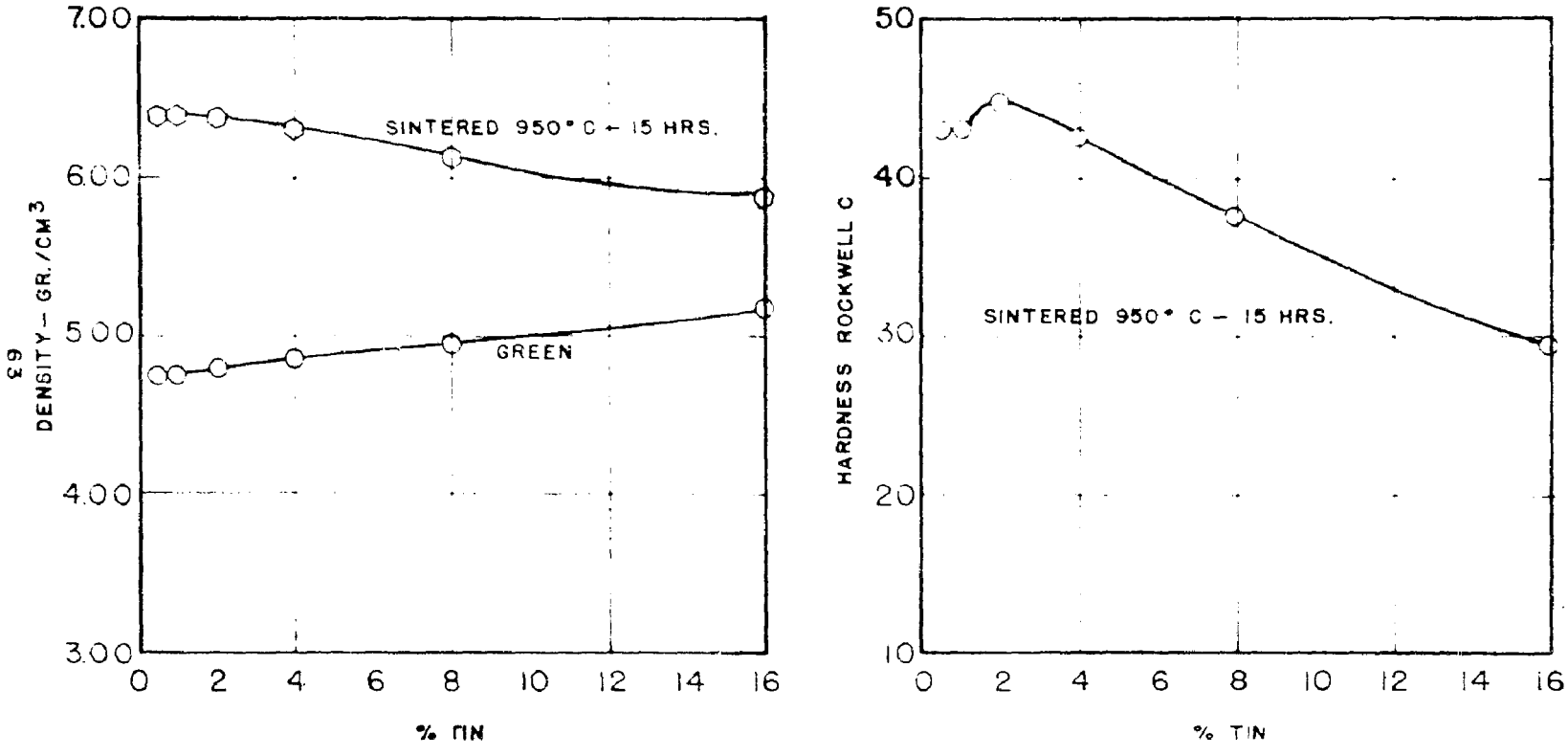
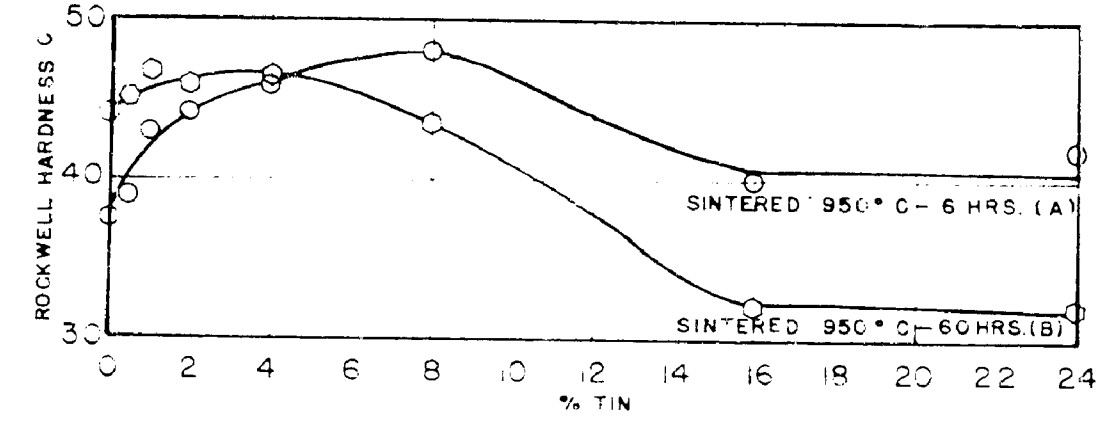


FIGURE 4
EFFECT OF TIN ON ZIRCONIUM (XYLENE MIX)



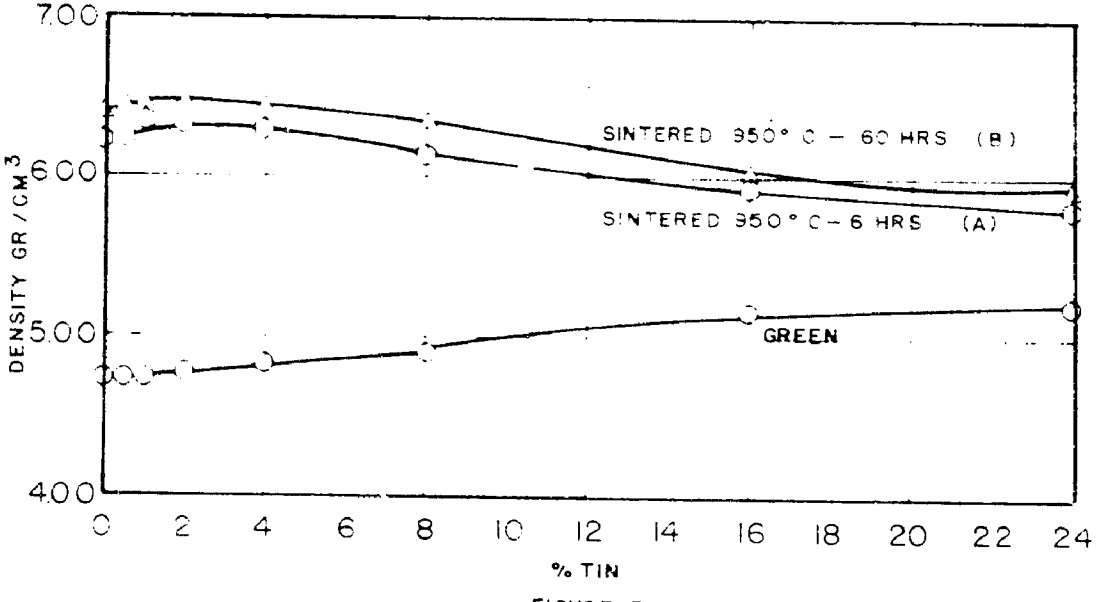


FIGURE 5
EFFECT OF TIN ON ZIRCONIUM (DRY MIX)

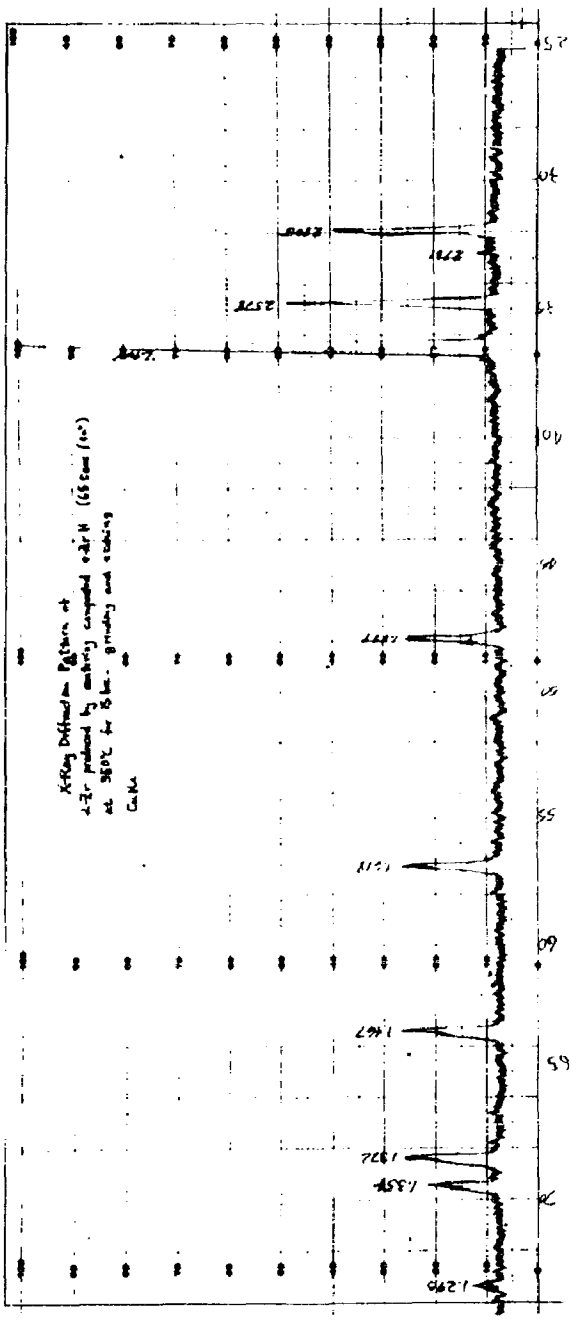


Figure 6

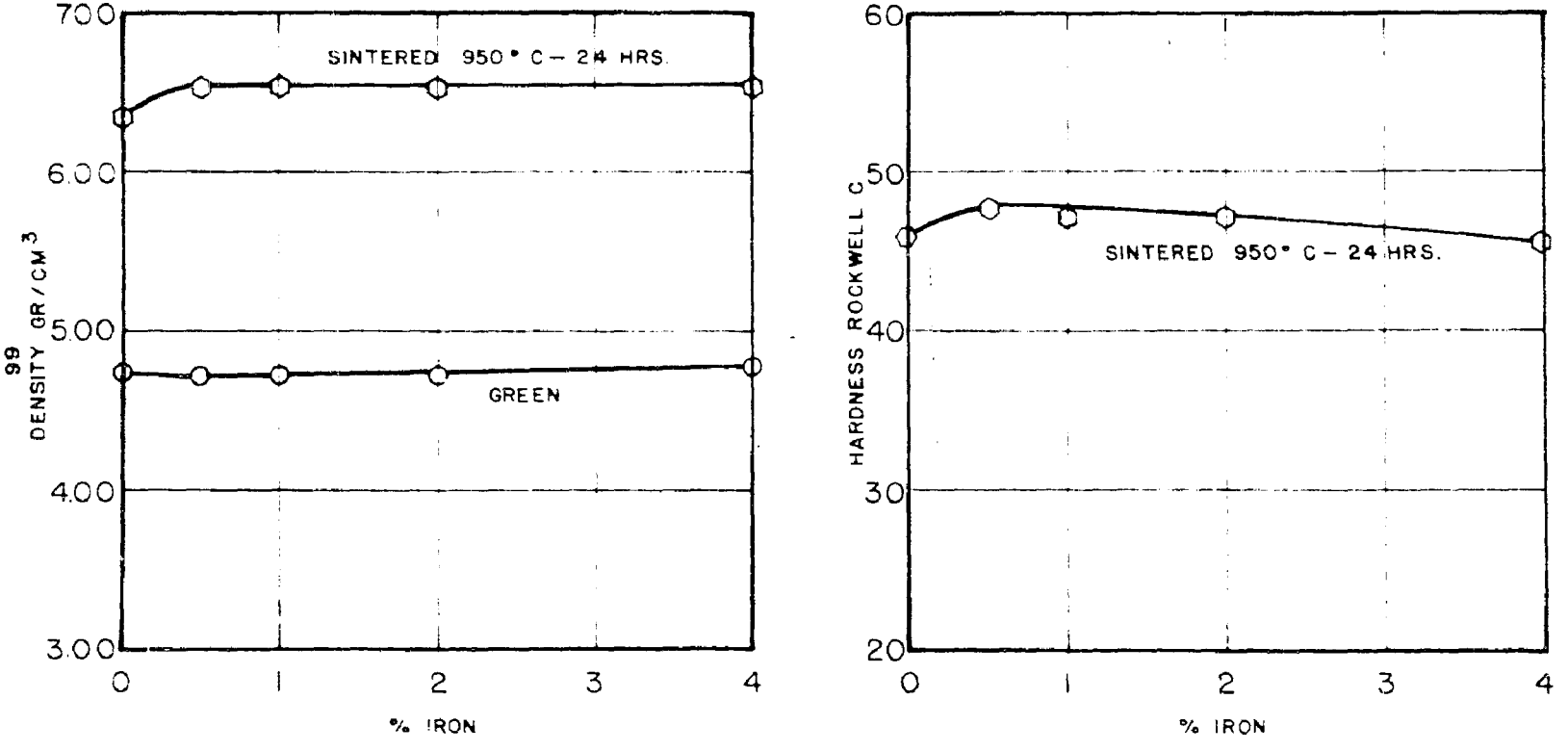


FIGURE 7
EFFECT OF IRON ON ZIRCONIUM

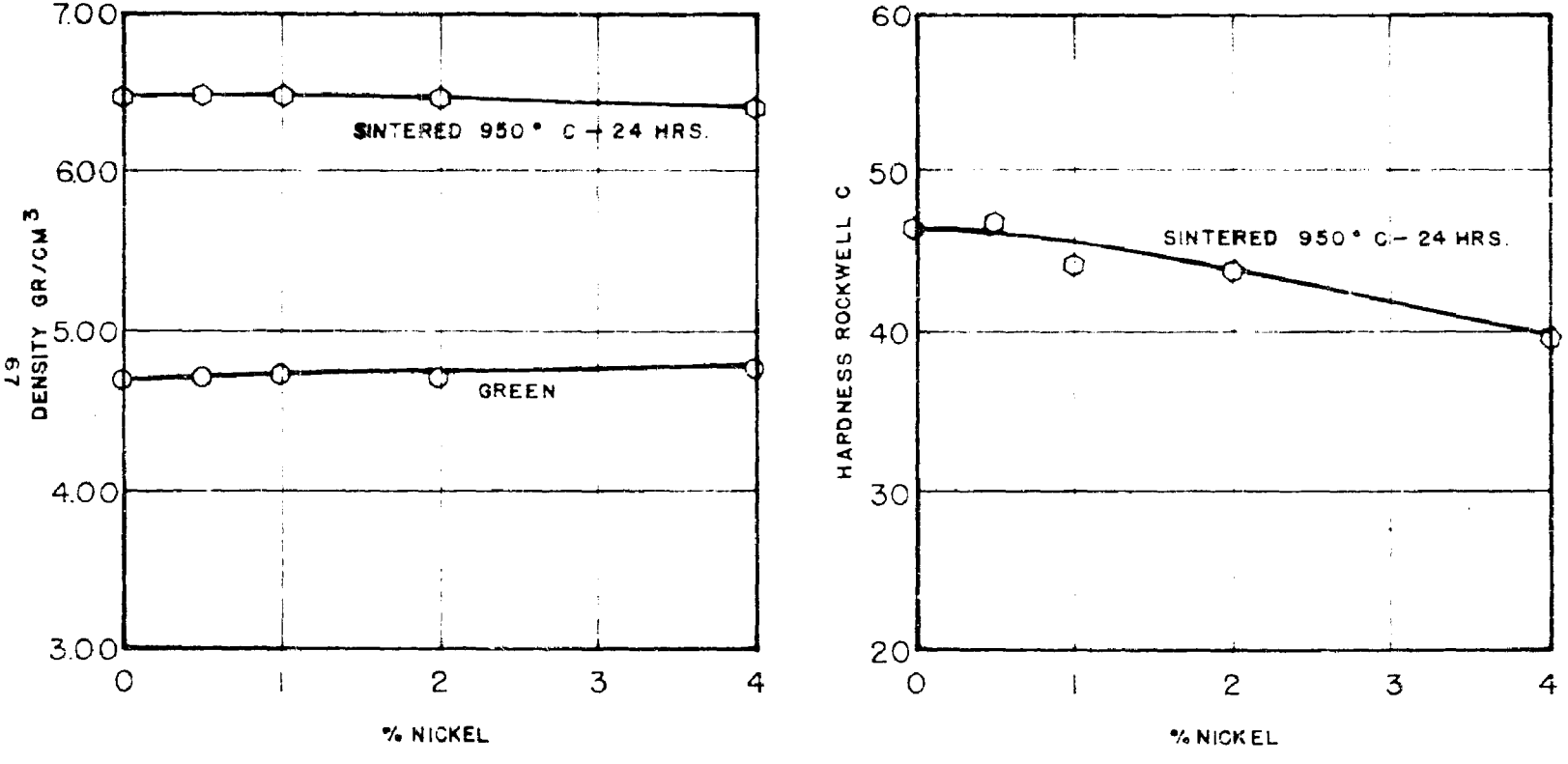


FIGURE 8
EFFECT OF NICKEL ON ZIRCONIUM

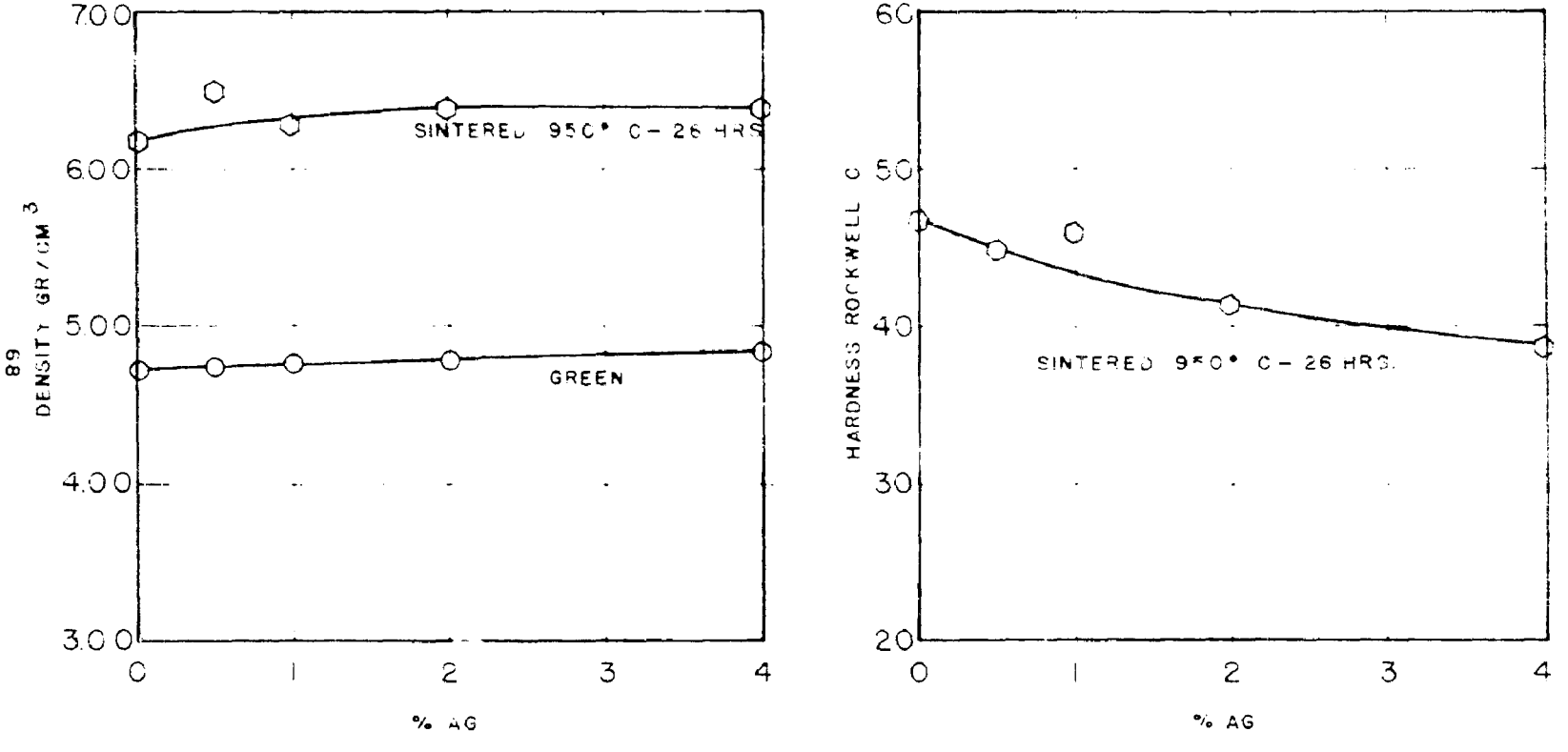


FIGURE 9
EFFECT OF SILVER ON ZIRCONIUM

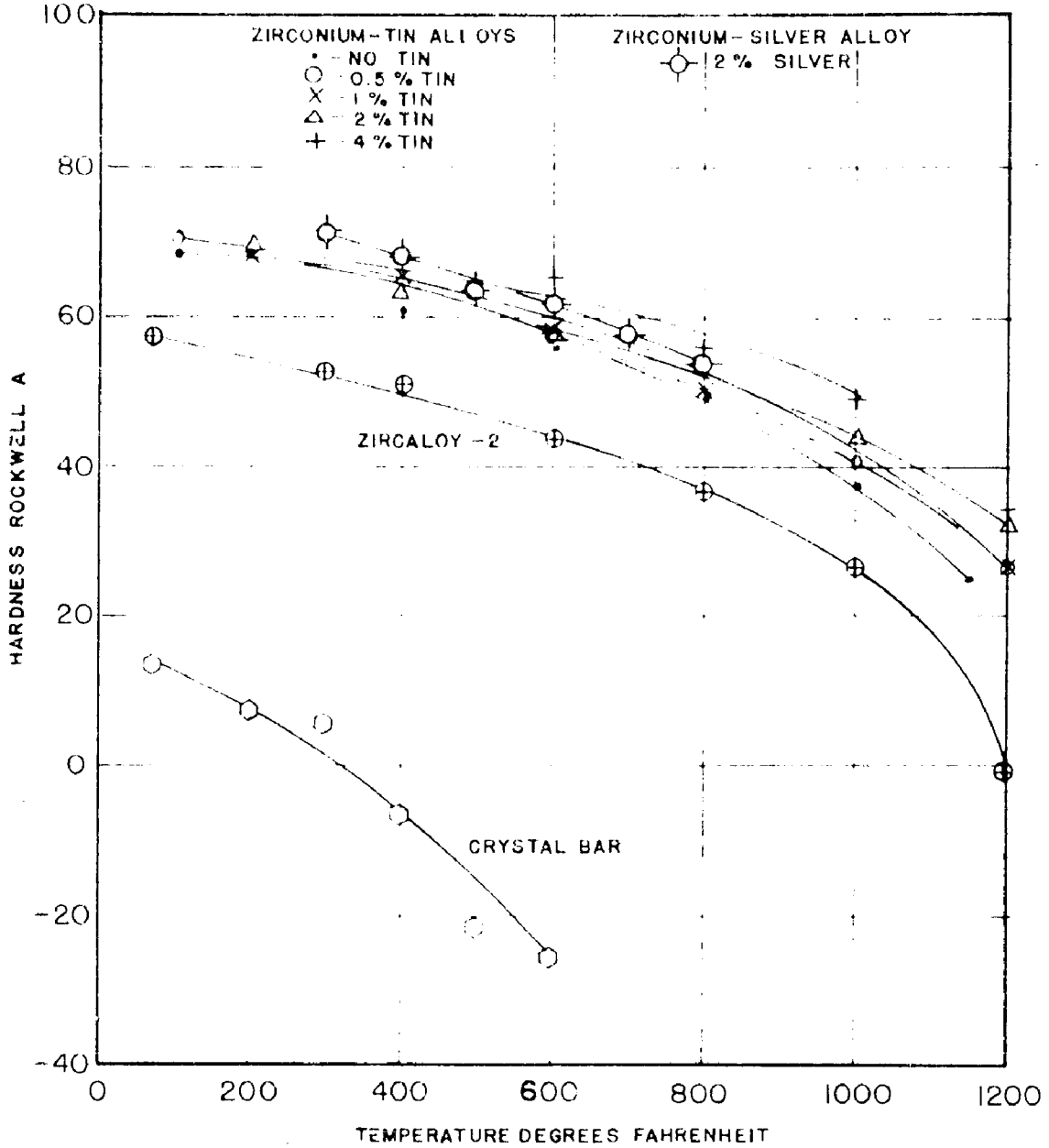


FIGURE 10

HOT HARDNESS OF PURE ZIRCONIUM AND SEVERAL ZIRCONIUM ALLOYS

PART IV

IRON POWDERS

MATERIALS:

Two types of iron powder were first examined to select one for further study. The Hoeganaes Sponge Iron Corporation supplied samples of their purest iron powder (Ancor 80) and of their finest iron powder (Ancor 200). The General Aniline and Film Corporation, Dyestuff and Chemical Division, Linden, New Jersey, supplied a sample of carbonyl iron powder (Grade L), batch B 20-16, PQ-23. On the basis of density obtainable in the sintered compact, the carbonyl iron powder was selected for further study.

Various additions were used as grain growth restrainers. They are: T.A.M. C.P. zirconia powder, Metal Hydrides Company Grade E zirconium hydride powder, Metals Disintegrating Company MD 105 copper powder, and Reynolds #400 atomized aluminum powder. Thorium oxide, Code 112, was purchased from Lindsay Chemical Company of West Chicago, Illinois. Cerium oxide, Lot No. 670, was purchased from Research Chemicals, Inc., Burbank, California, as was neodymium oxide, Lot No. 688, gadolinium oxide, (98%), Lot No. 680, dysprosium oxide, (98%), Lot No. 677, and lanthanum oxide, (99%), Lot No. 686.

PROCEDURE AND RESULTS:

Development of Basic Procedure

Since the purpose of this study is to evaluate the effect of nonmetallic particles in controlled additions to metals on the strength and grain structure, metal powders of high purity are required. Furthermore, to minimize the effect of porosity a high density sintered product was desired. A preliminary experiment

was run on three iron powders. The data (Table I) show the marked improvement in density obtained in the carbonyl iron.

The general procedure followed throughout this work with carbonyl iron was:

1. press at low pressure
2. sinter to produce high shrinkage in an atmosphere that will first reduce the oxide on the metal surfaces and then will degas the metal
3. repress at high pressure
4. resinter in atmosphere as (2).

The way a reducing-degassing atmosphere combination was attained was to add several specimens of pressed zirconium hydride. The volume of hydrogen (STP) released from a 40-gram compact of ZrH is 4,875 cm^3. The release of hydrogen begins when the evacuated system is heated above 400°C and continues up to the sintering temperature. The total pressure rises to over 1 mm of mercury. After several hours the original vacuum of 10^{-4} mm is again attained (10^{-5} mm at room temperature). The zirconium metal then remaining acts as a getter for any remaining gases in the system.

Copper additions were made to both the sponge iron and the carbonyl iron powders (Tables II and III), and although an improvement in strength was noted, the ductility was decreased, and it was decided not to use the alloy base for nonmetallic additions. The reason for the lack of improvement with copper was the limitation on sintering temperature. Sintering could not be done at a high enough temperature to achieve liquid phase bonding by the copper. Aluminum was tried also but yielded poor results.

It was thought that a novel modification of the method of internal oxidation for dispersing an oxide phase throughout a metal matrix would be to mix in zirconium hydride powder; during vacuum sintering the hydride is decomposed - any oxide on the metal particles is reduced by the hydrogen, and the zirconium produced acts as a getter for the water vapor produced, being thus converted to oxide itself.

An experiment was conducted with tensile bars in which the added zirconium hydride content varied from 0 to 4 per cent by weight. The data of Table IV show that a 1 per cent addition was effective in raising the strength by 20 per cent without loss of ductility. As can be seen from the photomicrographs of Figure 1, the addition of 1 per cent ZrH resulted in marked resistance to grain coarsening. Beyond this amount the grain size was even finer but the material suffered greatly in ductility. The very coarse grained specimens showed markedly irregular deformation. The 2 and 4% Zr-containing specimens displayed brittle fracture.

Another experiment was run in which Cu and ZrH were added, but the examination was confined to grain size measurements. The grain growth restraining ability of the Zr addition became less the higher the sintering temperature, as shown in Table V and in Figure 2. The copper addition had no grain growth restraining effect since the sintering temperature was not high enough to cause it to flow; the copper remained as discrete particles partially diffused into the surrounding iron.

The effect of zirconium oxide added directly as zirconia, rather than through the device of internal oxidation of zirconium,

was determined. The data are given in Table VI and in Figure 3. It will be noted that the zirconia directly added was not as effective a grain growth restrainer as was the zirconium oxide produced by internal oxidation.

J Series

The following mixes were prepared:

Identification	Carbonyl Iron Powder	Addition
J1	100%	None
J2	99%	1% Zirconia
J3	99%	1% Thoria

Specimen slugs, 1/4 inch diameter x 3/8 in. long, were pressed at 75 tons per square inch and sintered for four hours at 700°C. They were then repressed at 75 t.s.i. and examined (Ja series). Sintering was carried out at 700°C, using a programmed cycle of: heat to 700°C at 400°F per hour, hold for 4 hours at 700°C, cool at 400°F per hour. Hydrogen at approximately 100 mm pressure was the atmosphere.

The following series of specimens were examined:

Identification	Number of Heating Cycles In Addition to First Sinter
Ja	0
Jb	1
Jc	2
Jd	4
Je	8
Jf	11

Photomicrographs of some typical structures at 100X are given in the accompanying Figures 4 and 5.

The grain sizes were estimated by comparison with grids made according to the ASTM grain size charts, i.e., the grain size number, n, is defined by the expression: Number of grains per square inch at 100 magnification equals 2^{n-1} (Table VII).

The sintering was done in the alpha ferrite region, and as a result, the grain sizes were, in general, very small. The grains of sinterings made from the carbonyl iron powder without additions gradually coarsened from a very fine size to a fine size. The grains of the sintering that contained zirconia behaved similarly; but the specimens that contained thoria experienced a different grain growth pattern. Most of the grains remained very fine, and a small fraction grew to a size that was relatively much larger.

It is not known whether this effect of the thoria was due to a lack of uniform blending, or to partial solution of the compound in some of the iron grains. It did act, for the most part, as a very effective barrier to grain growth.

K Series

The following mixes were prepared:

Identification	Carbonyl Iron Powder	Addition
K1	100%	None
K2	99%	1% Zirconia
K3	99%	1% Thoria

Specimen slugs, 1/4 inch diameter by 3/8 inch long, were pressed, using stearic acid as a die lubricant, at 75 tons per square inch (tsi) and sintered for four hours at 900°C. They were then repressed at 75 tsi and resintered at 950°C for four hours before being examined (Ka series). Sintering was carried out at 950°C using a programmed cycle of:

1. Heat to 950°C at a rate of 205°C per hour.

2. Hold for four hours at 950°C.

3. Cool to room temperature at a rate of 205°C per hour.

The atmosphere during sintering was a low partial pressure of hydrogen during the first part and a vacuum for the balance of any given sintering operation. The partial pressure of hydrogen was obtained by charging a zirconium hydride briquet along with the samples to be sintered. The furnace chamber was evacuated, then heated. At 400°C the zirconium hydride began to decompose, the hydrogen reduced the oxides and the zirconium remaining reacted with the water produced to form zirconium dioxide and hydrogen.

The iron samples were all coarse-grained. There was no grain growth barrier effect noted in either the specimens containing zirconia or those containing thoria. The grain size was large (ASTM << 1 after 128 hours).

There was no noticeable decrease in porosity due to sintering. This was surprising in view of the results of Cizeron and Lacombe.(1) They found that the pores disappeared in a sample of carbonyl iron pressed at 21 tsi and sintered 785 hours at 895°C. They concluded that sintering in the alpha range, because of the fine grain size, permitted pore elimination; sintering in the gamma range produced coarse grains and the pore volume was large.

It is necessary to plastically deform the sinterings before the porosity can be reduced if the exceedingly long sintering times are to be precluded.

---

(1) G. Cizeron and P. Lacombe, Comptes rendus, July 25 (1955) 409.

LOG OF K SAMPLES

OPERATION	TOTAL NO. OF CYCLES
1st Sinter (one cycle)	
REPRESS	
2nd Sinter (one cycle) Ka1, Ka2, Ka3, Removed	1
3rd Sinter (one cycle) Kb1, Kb2, Kb3, Removed	2
4th Sinter (two cycles) Kc1, Kc2, Kc3, Removed	4
5th Sinter (four cycles) Kd1, Kd2, Kd3, Removed	8
6th Sinter (eight cycles) Ke1, Ke2, Ke3, Removed	16
7th Sinter (16 cycles) Kf1, Kf2, Kf3, Removed	32

M, N, O Series

The following mixes were prepared:

Identification	Carbonyl Iron Powder	Addition
M1	100%	None
M2	99%	1% Zirconia
M3	99%	1% Thoria
N1	100%	None
N3	99%	1% Thoria
O1	100%	None
O3	99%	1% Thoria

Batches of 500 grams of the mix were milled with flint balls in a quart-size porcelain jar for one hour. This time had been determined to be the optimum by a study of the thorium content, using X-ray fluorescent spectrography, of several samples taken after each of several milling periods.

A carbide (Kennametal K94) pellet die was used for the 1/4 inch diameter specimens, and a Haller steel die was used to prepare the tension test specimens. (Metal Powder Association Standard 10-50, pressure area 1.0 square inch.) The MPA specification calls for a compaction to 0.200 - 0.250 in. thickness.

The first pressing was done under a relatively low pressure (25-30 tons per square inch) and the repressing after the first sinter was done under a relatively high pressure (75-80 tons per square inch). The first sinter was done under a dry hydrogen atmosphere to reduce any oxide present, and subsequent sinterings after the repressing operation was carried out under vacua of 10^{-4} mm Hg.

The results are shown in Tables VIII through XI.

The density variations of the small pellets of the M Series were fairly pronounced. Sintering time had little effect (from 4 to 68 hours at 850°C) on the density of any of the compositions. The oxide additions lowered the density of iron; considering the data for the longest sinter, the pure iron sample had 96.1% of theoretical density (7.86), the iron + 1% ZrO_2 sample had 91.6% of theoretical (7.85), and the iron + 1% ThO_2 sample had 94.2% of theoretical (7.88).

As shown by the photomicrographs of Figures 6 and 7, there was very little change in porosity amoung the specimens. The ferrite grain, however, was considerably finer in the oxide-bearing iron than in the pure iron.

The tensile bars of the N Series were processed in the same way as were the samll cylinders of the M Series. Again, there was no regular influence of sintering time on the strength of ductility of the specimen. The densities were higher and showed an increase with increase in sintering time. Thoria slightly increased the tensile strength and decreased the elongation. The cold working of the tensile test raised the hardness from 10-15 to 60-80 Rockwell B. In the few tests made of the high temperature strength no significant advantage due to the thoria was found.

A modification was made in the processing of the O Series tensile bars. It was realized that if repressing were to be of value in reducing porosity a fair amount of plastic flow would have to take place. After the first pressing and the sintering in a hydrogen atmosphere the bars were placed in the tensile-bar die cavity at 90 degrees to the usual position and pressed to 80 t.s.i.

In the gage portion the bar spread from 0.180 to 0.225, and in the grip portion from .180 to .343. The bulk of the deformation took place at pressures of 30,000 for the iron and 45,000 for the iron plus thoria. Subsequent sintering yielded significantly higher densities. After 122 hours at 905°C the iron had reached 99.4% of maximum density. The microstructure of Figure 8 shows that the specimen was practically free of pores. Carbon pickup, probably from the stearic acid lubricant, was close to 0.10% at the surface, as shown by the photomicrograph of Figure 9. There was no carbon pickup discernible in the specimen containing thoria.

When loaded to 50-60% of their room temperature tensile strength, the oxide specimens ruptured in about half an hour at 1000°F, about two to four hours at 800°F, and at least 150 hours at 700°F.

In those tensile bars in which the grain was coarse, as in the carbonyl iron specimens sintered at 950°C, plastic flow during the test was accompanied by a marked roughening of the surface. Surfaces of several fractured test bars are shown in Figure 10.

P and R Series

Identification	Carbonyl Iron Powder	Addition
P	100%	None
R	99%	1% Ceria

Batches of 500 grams of the one per cent cerium oxide mix were milled with flint balls in a quart-size porcelain jar for one hour.

A Haller steel die was used to prepare the tension test specimens. (Metal Powder Association Standard 10-50, pressure area 1.0 square inch.) The MPA specification calls for a compaction to 0.200 - 0.250 inch thickness.

The first pressing was done under a relatively low pressure (25 tons per square inch) and the repressing after the first sinter was done under a relatively high pressure (80 tons per square inch). The specimens were turned 90 degrees in the die for the repressing.

The first sinter was carried out under a dry hydrogen atmosphere to reduce any oxide present, and, after the repressing operation, the second sinter was carried out under a vacuum of 10^{-4} mm Hg. The temperature of the first sinter, in all cases, was 950°C, and the time was 1 hour. The temperatures of the second sinter were 850°C and 950°C, and the time was 150 hours.

Both the room temperature and elevated temperature tensile tests were made on a Baldwin lever arm creep test machine. The specimens were placed in the machine, slightly pre-loaded, brought up to the testing temperature and held at this temperature for 1/2 hour, and then pulled to destruction in approximately 15 minutes.

The data are presented in Tables XII through XVI and plotted in Figure 11.

In general, the effect of raising the temperature of the tensile test of the pure iron specimens was to lower the short-time tensile strength. In the specimens containing 1% ceria, however, a pronounced age hardening effect was noted over the range of 200-400°F. This hardening was particularly pronounced in the specimens sintered at 850°C.

Ceria definitely improved the high temperature strength properties of the specimens sintered at 850°C, but had a negligible effect on the high temperature strength of the specimens sintered at 950°C. While the ductilities of both sets of ceria specimens were very low at room temperature, they were much higher at temperatures of 200°F and above in the specimens sintered at 850°C; the gain in ductility at the higher testing temperature of the specimens sintered at 950°C was very slight.

In both sets of specimens, i.e., pure iron and iron plus 1% ceria, the group sintered at 850°C was much stronger and had higher ductility than the group sintered at 950°C.

The photomicrographs of Figures 12 and 13 disclose the fact that the ceria addition had very little effect on preventing the grain growth of the iron. This is in marked contrast to the effect of thoria (J Series of this Report). Thoria not only resulted in grain refinement in the specimens sintered high in the alpha region (850°C), but also in the specimens sintered in the gamma region (950°C).

Part of the reason for the relative ineffectiveness of ceria as a grain growth restrainer is probably its relatively coarse particle size. It does appear, however, that the ceria particles coalesced during the 950°C sinter; and it appeared that the thoria particles, discussed in the previous report, coalesced only slightly by raising the sintering temperature 100°C.

Figure 12a shows that the pure iron specimen was almost free of porosity, and the density data of Table XVI confirm this observation (99.7% of theoretical density).

PI, Tc, U and W Series

Identification	Carbonyl Iron Powder	Addition
PI	100%	None
Tc	99%	1% Neodymia
U	99%	1% Dysprosia
W	99%	1% Gadolinia

Tensile test specimens were prepared by the procedure described for the P and R series. Stearic acid was used as the die lubricant; the second sinter was carried out at just one temperature, 850°C.

A mix containing 1% lanthana was also prepared. However, the tensile test specimens which were pressed from the mix broke from the slightest stress and were not tested.

The data which were obtained are presented in Tables XVII through XX and Figure 14.

The tensile strength of the oxide additions did not differ much from that of pure iron, with the exception of the gadolinia mixture. Up through 600°F its tensile strength was consistently higher than any of the other mixes and pure iron, but at 800°F its tensile strength dropped below that of pure iron.

The neodymia specimens exhibited a much lower elongation than the others at all temperatures tested. The gadolinia specimens had a lower elongation than pure iron and approximately paralleled that of iron until 800°F was reached, at which temperature the gadolinia mix showed greater elongation than pure iron. The elongation properties of the dysprosia specimens were erratic, at some temperatures higher than pure iron and at others lower than pure iron.

TABLE I

Density and Hardness of Sintered Iron Compacts
(1 1/2 in. Diameter)

(Hydrogen + Vacuum Sintering)
Pressing Pressure: 65 tons/sq.in.
Sintering Conditions: 15 hrs. at 720°C + 6 hrs. at 925°C

Type	Density gr/cm^3	Hardness RB
Anchor 200	7.24	42
Anchor 80	7.16	34
Carbonyl	7.42	10

TABLE II

Effect of Copper on the Hardness and Strength of Sintered Iron
(Anchor 200 Iron and MD 105 Copper)

Processing: (Hydrogen and Vacuum Sintering)
Mixes blended in ball mill, pressed at 30 tons per sq. in., sintered 14 hrs. at 700°C, repressed at 65 tons per sq. in., final sintering-4 hrs. at 910°C.
Lubrication: Lubriplate

% Copper	Tensile Strength psi	Elongation % in 1 in.	Hardness RB
0	33,700	16	32
1	47,800	10	60
2	45,600	8	61
4	45,600	8	61
8	45,100	8	61

TABLE III

Effect of Copper and Aluminum
On The Hardness and Strength of Carbonyl Iron

Processing: (Hydorgen and Vacuum Sintering)
Mixes blended in ball mill, pressed at 30 t.s.i., sintered 48 hrs. at 700°C, repressed at 65 t.s.i., final sintering-4 hrs. at 910°C.
Lubricant: Lubriplate

% Element	Tensile Strength psi	Elongation % in 1 in.
1-Cu	42,100	31
1-Al	27,850	5

TABLE IV

Effect of Zirconium Additions on
The Strength of Sintered Carbonyl Iron

Processing: (Hydrogen and Vacuum Sintering)
Mixes blended in ball mill, pressed at 30 t.s.i., sintered 2 hrs. at 720°C, repressed at 65 t.s.i., final sintering-12 hrs. at 925°C, 1 hr. at 995°C, 1 hr. at 1065°C.
Lubricant: Lubriplate

% ZrH Added	Tensile Strength psi	Elongation in 1 inch	Hardness RB
None	30,700	37.5	10
0.5	32,400	30.0	12
1.0	37,000	36.0	28
2.0	30,400	8.0	20
4.0	37,600	8.0	30

TABLE V

Effect of Copper and Zirconium on the Grain Size of Carbonyl Iron

Processing: (Hydrogen and Vacuum Sintering)
No Lubrication; mixes blended in ball mill, pressed 30 t.s.i. 1/4 in. diameter die, sintered 16 hrs. at 705°C, repressed 75 t.s.i.
2nd sinter: 20 hrs. at 870°C
3rd sinter: 14 hrs. at 925°C
4th sinter: 20 hrs. at 1000°C

Addition	ASTM Grain Size After:		
	2nd Sinter	3rd Sinter	4th Sinter
None	6	3	3
1% Cu	3	3	3
1% ZrH	7	4	4

TABLE VI

Effect of Zirconia on the Grain Size of Carbonyl Iron

Processing: (Hydrogen and Vacuum Sintering)
No lubrication; mixes blended in ball mill, pressed 30 t.s.i. 1/4 in. diameter die, sintered 15 hrs. at 775°C repressed 75 t.s.i.
2nd sinter: 11 hr. at 910°C
3rd sinter: 20 hr. at 935°C
4th sinter: 35 hr. at 955°C

Addition	ASTM Grain Size After:				Density, gr/cm^3
	1st Sinter	2nd Sinter	3rd Sinter	4th Sinter	After 4th Sinter
None	8	<1	<1	<1	7.57
1% ZrO_z	9	<1	<1	<1	7.57

TABLE VII

Grain Size Values
(ASTM Grain Size Numbers)

Treatment	Carbonyl Iron Alone		With 1% ZrO_2		With 1% ThO_2	
As pressed 75 t.s.i. sintered 1 cycle* repressed 75 t.s.i.	Ja1		Ja2		Ja3	
	80%	12-13	50%	12-13	80%	12-13
	20%	8- 9	50%	9-10	18%	7- 8
					2%	6
As above sintered 1 cycle	Jb1		Jb2		Jb3	
	100%	7- 8	80%	9-10	80%	12-13
			20%	5- 6	20%	5- 6
2 cycles	Jc1		Jc2		Jc3	
	90%	9	90%	7- 8	80%	11-12
	10%	6- 7	10%	5- 6	50%	5- 6
4 cycles	Jd1		Jd2		Jd3	
	50%	7- 8	10%	11-12	50%	12-13
	30%	6- 7	70%	7- 8	20%	7- 8
	20%	5- 6	20%	5- 6	30%	5- 6
8 cycles	Je1		Je1		Je1	
	50%	6- 8	80%	8- 9	70%	11-12
	50%	5- 6	20%	5- 6	30%	6- 7
11 cycles	Jf1		Jf2		Jf3	
	60%	7- 8	60%	7- 8	60%	12-13
	40%	6- 7	40%	5- 6	40%	5- 6

*A cycle consisted of a program sinter at a heating rate of 400°F per hour to 1290°F, a 4 hour hold at 1290°F, and a cooling rate to room temperature of approximately 400°F per hour.

TABLE VIII

M Series

M1 - Carbonyl iron

M2 - Carbonyl iron plus 1% zirconia

M3 - Carbonyl iron plus 1% thoria

Processing

1. Mixes ball milled one hour
2. Cylinders 0.250 inch diameter x 1/2 inch high pressed at 35 tons per square inch (stearic acid lubricant)
3. Compacts sintered 4 hours at 850°C, in vacuum
4. Sinterings repressed at 70 tons per square inch
5. Specimens resintered at 850°C, in vacuum

Ma - 4 hours
Mb - 8 hours
Mc -16 hours
Md -32 hours
Me -48 hours
Mf -68 hours

Density

Sinter Time Hours	Pure Iron gr/cc	% of Theo-retical	Iron Plus 1% ZrO_2	% of Theo-retical	Iron Plus 1% ThO_2	% of Theo-retical
4	7.52	95.7	7.12	90.7	7.31	92.8
8	7.54	96.0	7.39	94.1	6.95	88.2
16	7.67	97.6	7.44	94.8	7.45	94.5
32	7.48	95.2	7.25	92.4	7.29	92.5
48	7.52	95.7	7.38	94.0	7.30	92.6
68	7.55	96.1	7.19	91.6	7.43	94.3

TABLE IX

N Series

N1 - Carbonyl iron

N3 - Carbonyl iron plus 1% thoria

Processing

1. Mix ball milled one hour
2. Tensile bars pressed at 35 tons per square inch (stearic acid lubricant)
3. Compacts sintered in hydrogen atmosphere 4 hours at 850°C (bright)
4. Sinterings repressed at 70 tons per square inch
5. Specimens resintered at 830°C, in vacuum

Na - 4 hours
Nb - 8 hours
Nc - 16 hours
Nd - 34 hours

Tensile Properties at Room Temperature

		Pure Iron		Iron plus 1% ThO_2	
Specimen	Sinter Time, Hrs.	Tensile Strength p.s.i.	% Elongation in 2 in.	Tensile Strength p.s.i.	% Elongation in 2 in.
Na	4	35,350	37.5	35,350	25
Nb	8	35,950	35.0	37,050	30
Nc	16	33,800	34.0	35,600	27
Nd	34	35,700	32.5	35,550	30

Density

	Pure Iron		Iron plus 1% ThO_2	
Specimen	Meas.	% of Theor.	Meas.	% of Theor.
Na	7.64	97.2	7.26	92.1
Nb	7.62	97.0	7.44	94.4
Nc	7.73	98.4	7.54	95.7

TABLE X

N Series

Tensile Properties at Elevated Temperature

Sinter Time Hrs.	Specimen	
4	Pure Iron	Loaded at 60% of tensile, 0.5 hr. up to 950°F (part of grip end broke in jaws) Reloaded at 50% of tensile, 0.5 hr. up to 1000°F Elongation 55%
	Iron plus 1% ThO_2	Loaded at 50% of tensile, 0.4 hr. up to 1000°F Elongation 12.5%
8	Pure Iron	Loaded at 50% of tensile 0.25 hr. to 800°F and 1.75 hrs. at 800°F. Elongation 30%
	Iron plus 1% ThO_2	Loaded at 50% of tensile, 0.25 hr. to 800°F and 3.9 hrs. at 800°F. Elongation 32.5%

TABLE XI

O Series

O1 - Carbonyl iron

O3 - Carbonyl iron plus 1% thoria

Processing

1) Mix ball milled one hour

2) Tensile bars pressed at 35 tons per square inch (stearic acid lubricant)

3) Compacts sintered in hydrogen atmosphere 4 hours at 950°C (bright)

4) Sinterings repressed at 80 tons per square inch. The specimens were placed on edge and pressed to tensile bar shape. Most of the flow took place before 15 t.s.i. for iron and before 23 t.s.i. for the iron containing 1% thoria.

5) Specimens resintered:

Oa - 5 hours at 835°C, started out under vacuum, but belt on pump broke towards end of run, specimens scaled

Ob - 3 1/2 hours at 835°C in hydrogen (positive pressure 1 inch Hg) specimens bright
Total time 8 1/2

Oc - 8 hours at 950°C in vacuum
specimens bright Total time 16 1/2

Od - 14 1/2 hours at 950°C in vacuum
specimens bright Total time 31

Oe - 91 1/2 hours at 950°C in vacuum
specimens light grey, vacuum etched
Total time 122 1/2

TABLE XI (continued)

O Series

Tensile Properties at Room Temperature

Sinter Conditions	Pure Iron Tensile Strength psi	% Elongation In 1"	% Elongation In 2"	Iron plus 1% ThO_2 Tensile Strength psi	% Elongation In 1"	% Elongation In 2"
Oa) 5 hrs. @ 835°C lost vacuum, Specs. scaled	35,250		31.5	38,150		25
Ob) Additional 3 1/2 hrs. @ 835°C in H_2 Specs. bright	35,150		35	37,650	32	21
Oc) Additional 8 hrs. @ 950°C in vacuum Specs. bright	35,000	48	30.5	39,000	42	27.5
Od) Additional 14 1/2 hrs. @ 950°C in vacuum Specs. bright	32,780	45	30	38,200	45	27.5
Oe) Additional 91 1/2 hrs. @ 950°C in vacuum Specs. grey	35,600	47	30	39,500	47	30

Density

Sample	Pure Iron Meas.	Pure Iron % of Theor.	Iron plus 1% ThO_2 Meas.	Iron plus 1% ThO_2 % of Theor.
Ob	7.69	97.8	7.70	97.8
Oc	7.76	98.8	7.74	98.2
Od	7.70	98.0	7.75	98.4
Oe	7.81	99.4	7.70	97.8

TABLE XII

Tensile Properties

Pa Series - Pure Iron
Sintered for 150 Hours at 850°C

Specimen No.	Temperature of Fracture	Tensile Strength (psi)	% Elongation 1 in.	% Elongation 2 in.
13	Room	32,750	40	26.5
6	Room	34,400	42	30
Avg.	Room	33,575	41	28.2
1	230°F	29,200	35	21.5
9	250°F	29,850	27	17
Avg.	240°F	29,525	31	19.2
2	400°F	26,600	40	25
11	400°F	28,100	27	17.5
Avg.	400°F	27,350	33.5	21.2
12	600°F	20,750	48	30.5
14	600°F	20,850	55	28.5
Avg.	600°F	20,800	51.5	29.5
19	800°F	19,500	79	55
15	800°F	15,950	45	33
Avg.	800°F	17,725	62	44

TABLE XIII

Tensile Properties

Pb Series - Pure Iron
Sintered for 150 Hours at 950°C

Specimen No.	Temperature of Fracture	Tensile Strength (psi)	% Elongation 1 in.	2 in.
29	Room	32,100	35	25
30	Room	31,400	33	24.5
Avg.	Room	31,750	34	24.7
33	200°F	24,000	28	20
31	200°F	25,550	35	23
Avg.	200°F	24,775	31.5	21.5
22	400°F	20,200	27	16.5
24	400°F	21,600	15	10
Avg.	400°F	20,900	21	13.2
26	600°F	15,850	20	12.5
35	600°F	18,500	29	20
Avg.	600°F	17,175	24.5	16.2
28	800°F	12,250	23	16
25	800°F	13,350	35	26
Avg.	800°F	12,800	29	21

TABLE XIV

Tensile Properties

Ra Series - Iron plus 1% CeO_2
Sintered for 150 hours at 850°C

Specimen No.	Temperature of Fracture	Tensile Strength (psi)	% Elongation 1 in.	2 in.
1	Room	23,250	2	1
9	Room	21,200	1	1
Avg.	Room	22,225	1.5	1
7	200°F	31,850	10	8
13	200°F	32,950	32	21
Avg.	200°F	32,400	21	14.5
6	400°F	32,400	25	15.5
12	400°F	31,200	23	14
Avg.	400°F	31,800	24	14.7
4	600°F	27,000	22	13.5
3	600°F	24,650	23	20
Avg.	600°F	25,825	22.5	16.7
11	800°F	20,200	27	16.5
2	800°F	19,450	17	15
Avg.	800°F	19,825	22	15.7

TABLE XV

Tensile Properties

Rb Series - Iron plus 1% CeO_2
Sintered for 150 hours at 950°C

Specimen No.	Temperature of Fracture	Tensile Strength (psi)	% Elongation 1 in.	2 in.
22	Room	16,400	3	2
24	Room	18,050	3	2.5
Avg.	Room	17,225	3	2.2
28	200°F	18,100	4	3.5
19	200°F	18,450	3	2
Avg.	200°F	18,275	3.5	2.7
20	400°F	19,050	5	4
23	400°F	19,650	5	4
Avg.	400°F	19,350	5	4
25	600°F	17,700	7	5
18	600°F	17,100	6	4.5
Avg.	600°F	17,400	6.5	4.7
27	800°F	14,700	10	7.5
16	800°F	13,800	15	10
Avg.	800°F	14,250	12.5	8.7

TABLE XVI

a. Density

Sintering Temperature	Pure Iron Measured	Pure Iron % of Theor.	Iron Plus 1% CeO_2 Measured	Iron Plus 1% CeO_2 % of Theor.
850°C	7.84	99.7	7.78	98.5
950°C	7.70	98.0	7.68	97.0

b. Average Hardness - Rockwell F

Sintering Temperature	Pure Iron	Iron Plus 1% CeO_2
850°C	59.3	71.6
950°C	44.9	58.1

TABLE XVII

Tensile Properties

PI Series - Pure Iron
Sintered for 150 Hours at 850°C

Specimen No.	Temperature of Fracture	Tensile Strength (psi)	% Elongation 1 in.	% Elongation 2 in.
4	Room	38,400	30	20
13	Room	38,400	38	20
2	Room	38,400	35	24
Avg.	Room	38,400	34	21
5	200°F	33,100	43	27.5
9	200°F	34,400	37	24
Avg.	200°F	33,800	40	26
12	400°F	33,200	35	23
14	400°F	31,800	30	19
Avg.	400°F	32,500	32	21
6	600°F	25,400	38	20.5
7	600°F	25,600	35	22.5
Avg.	600°F	25,500	36.5	21.5
10	800°F	19,800	30	24
1	800°F	18,500	34	25
Avg.	800°F	19,200	32	24.5

TABLE XVIII

Tensile Properties

Tc Series - Iron Plus 1% Nd_2O_3
Sintered for 150 Hours at 850°C

Specimen No.	Temperature of Fracture	Tensile Strength (psi)	% Elongation 1 in.	% Elongation 2 in.
14	Room	39,500	15	12.5
12	Room	38,200	20	15
15	Room	38,700	10	7.5
Avg.	Room	38,800	15	11.5
11	200°F	36,200	32	20
8	200°F	34,200	16	11
Avg.	200°F	35,200	24	15.5
1	400°F	29,200	18	12
4	400°F	29,100	34	21.5
Avg.	400°F	29,150	26	17
6	600°F	25,900	24	16
9	600°F	27,300	22	17.5
Avg.	600°F	26,600	23	17
3	800°F	18,600	15	12
7	800°F	22,200	35	23.5
Avg.	800°F	20,400	25	18

TABLE XIX

Tensile Properties

U Series - Iron plus 1% Dy_2O_3
Sintered for 150 Hours at 850°C

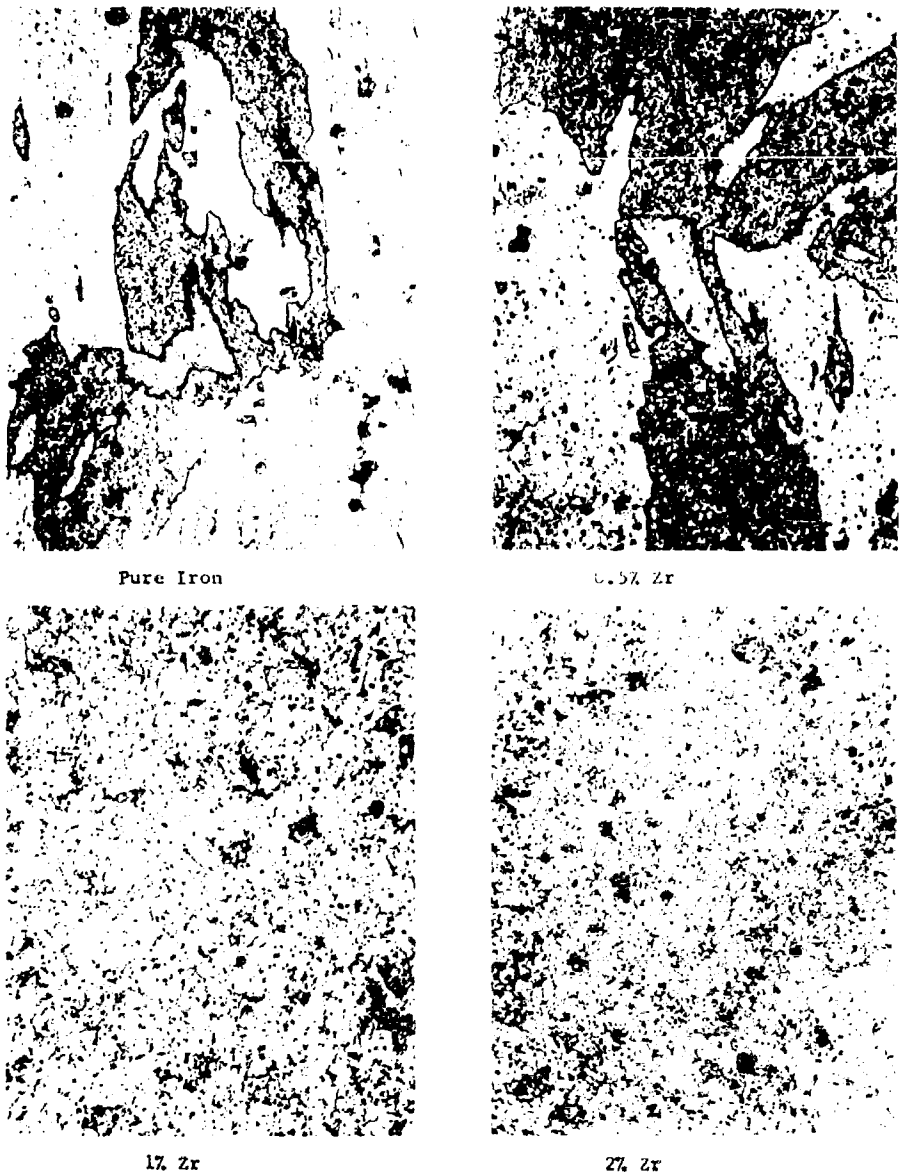
Specimen No.	Temperature of Fracture	Tensile Strength (psi)	% Elongation 1 in.	2 in.
2	Room	38,000	40	26.5
16	Room	39,000	38	22.5
3	Room	39,000	40	25
Avg.	Room	38,700	39.5	24.5
12	200°F	33,700	35	24
9	200°F	34,300	21	17.5
Avg.	200°F	34,000	28	21
5	400°F	29,700	34	22
10	400°F	29,800	36	22.5
Avg.	400°F	29,750	35	22
15	600°F	24,200	28	19
4	600°F	25,100	39	25
Avg.	600°F	24,600	33.5	22
13	800°F	18,500	38	26.5
7	800°F	17,500	40	27
Avg.	800°F	18,000	39	27

TABLE XX

Tensile Properties

W Series - Iron Plus 1% Gd_2O_3
Sintered for 150 Hours at 850°C

Specimen No.	Temperature of Fracture	Tensile Strength (psi)	% Elongation 1 in.	2 in.
8	Room	41,200	26	19
4	Room	40,600	26	17.5
5	Room	41,000	32	20
Avg.	Room	40,900	28	19
7	200°F	41,100	35	22
14	200°F	35,500	32	20
Avg.	200°F	38,300	33.5	21
16	400°F	32,800	29	19
15	400°F	32,500	27	17
Avg.	400°F	32,650	28	18
12	600°F	28,200	30	19
3	600°F	28,000	35	21.5
Avg.	600°F	28,100	32.5	20
13	800°F	19,150	22	15
11	800°F	18,100	27	16
Avg.	800°F	18,600	24.5	15.5



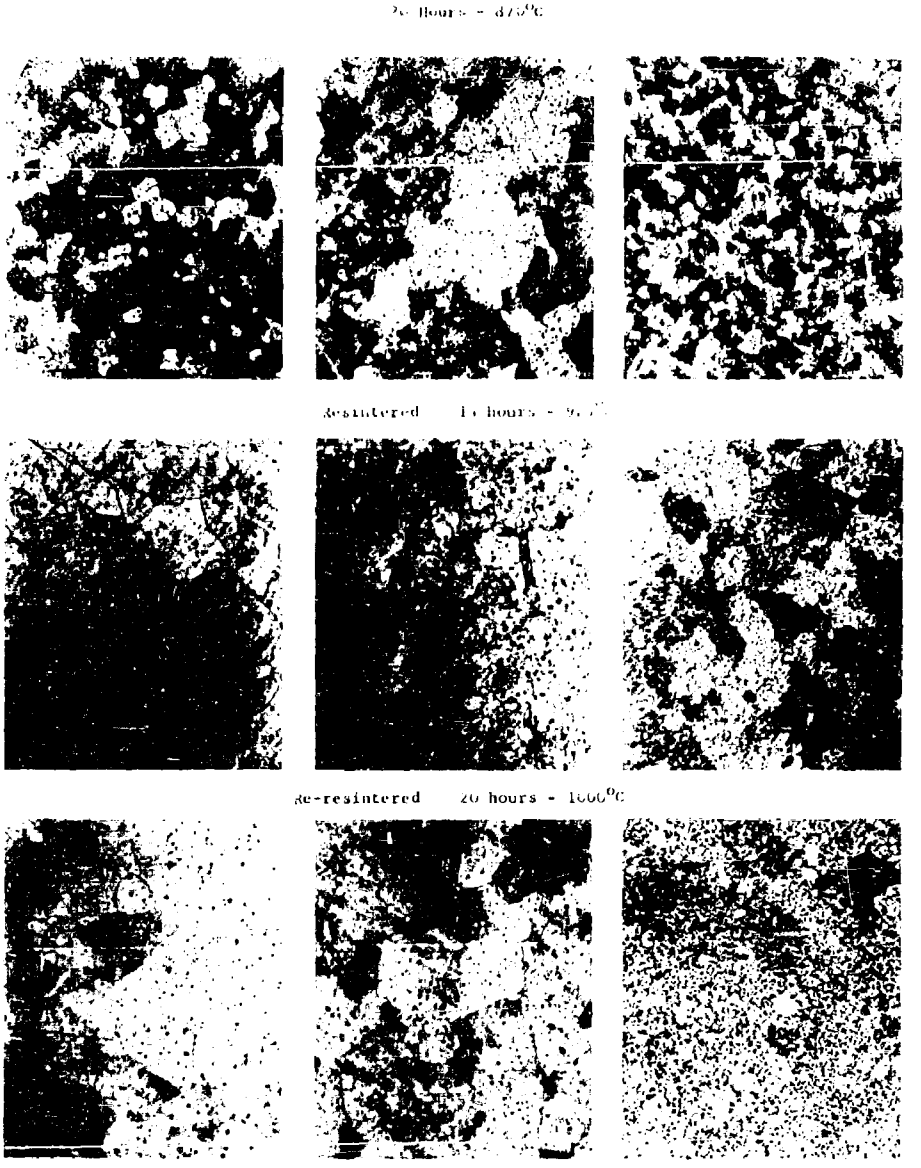
Pure Iron

0.5% Zr

1% Zr

2% Zr

Figure 1. Effect of Zirconium (added as ZrH) on the structure of tensile bars made from carbonyl iron. Powders 50X nital etch.



Pure Iron 1% Cu 1% Zr

Figure 2. Effect of Cu and of Zr on the Grain Size of Carbonyl Iron. 100X Nital etch.

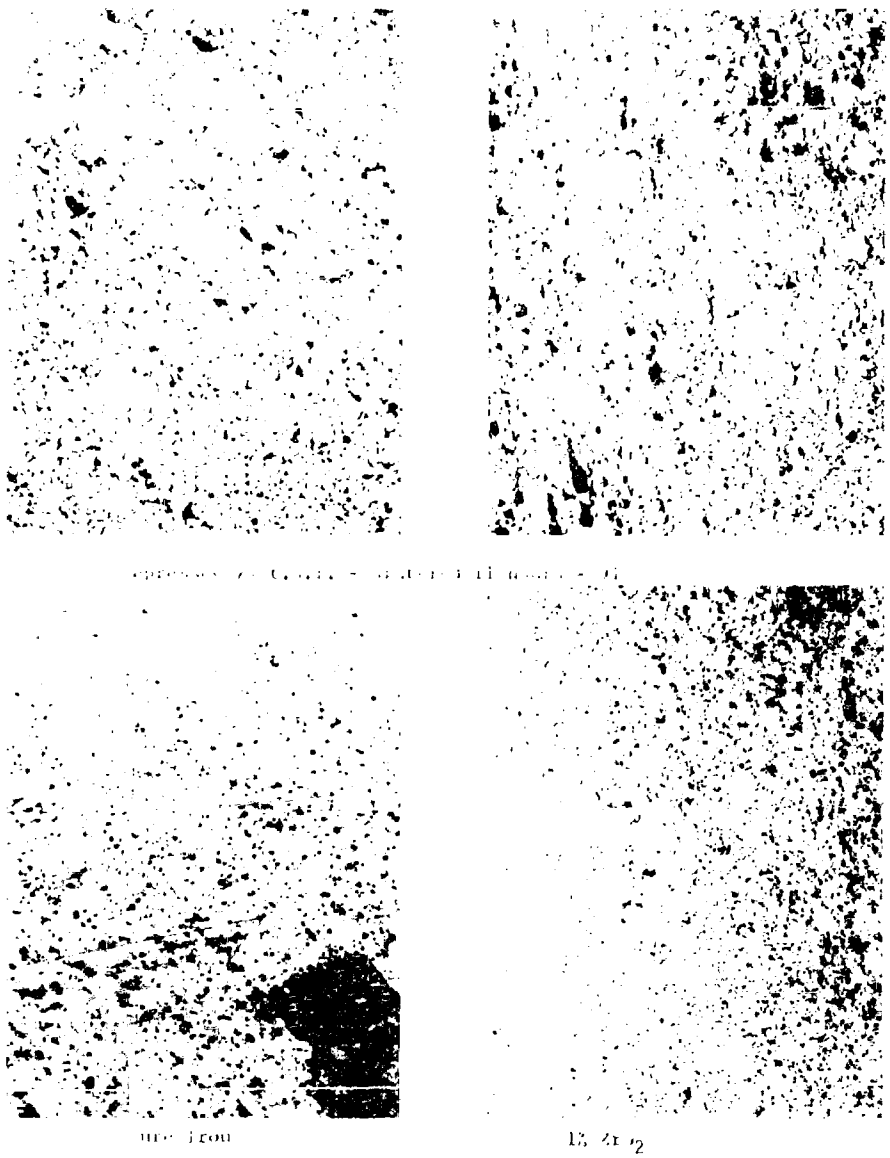
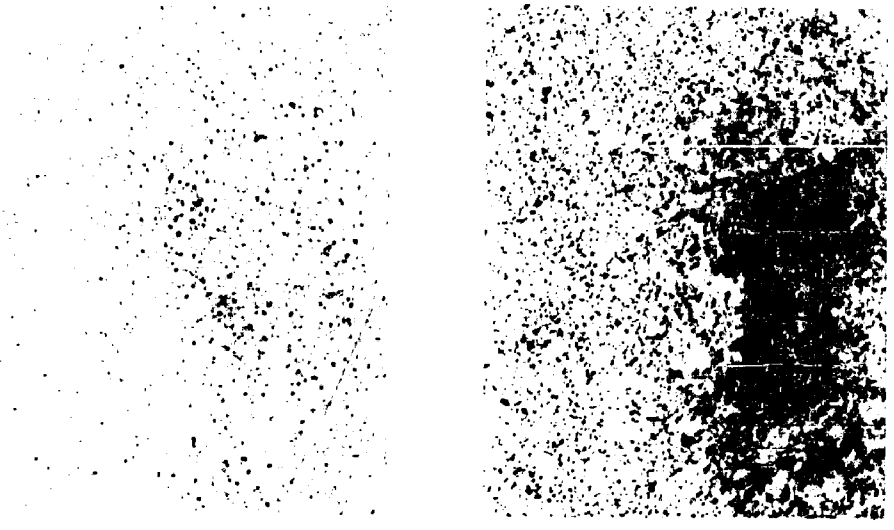
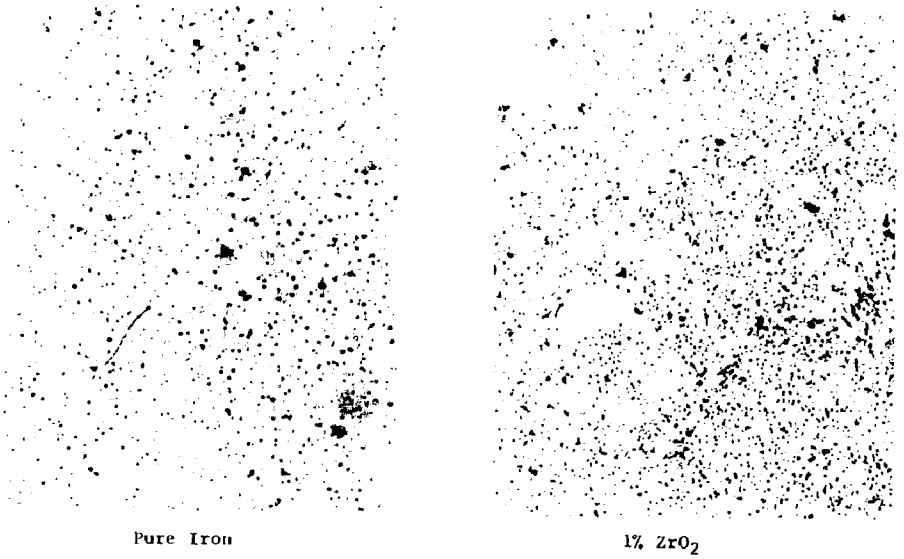


Figure 3.. Effect of Zirconia on the grain growth of carbonyl Iron, 100X Nital Etch.

Resintered 20 hours at 935°C



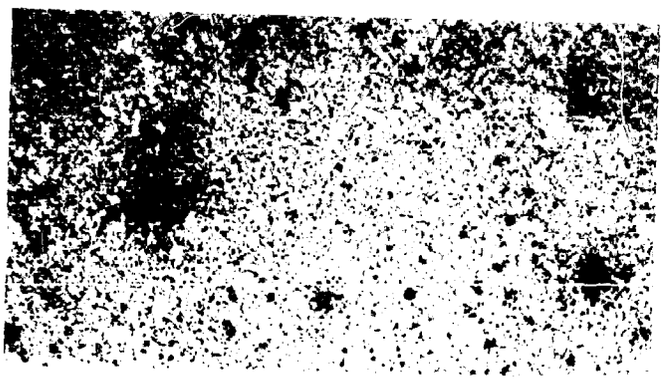
Re-resintered 35 hours at 955°C



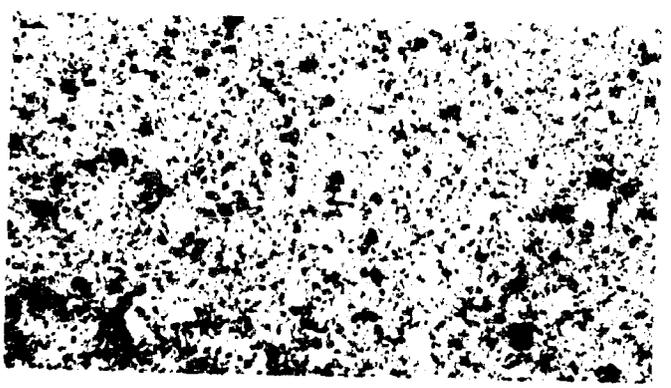
Pure Iron

1% ZrO_2

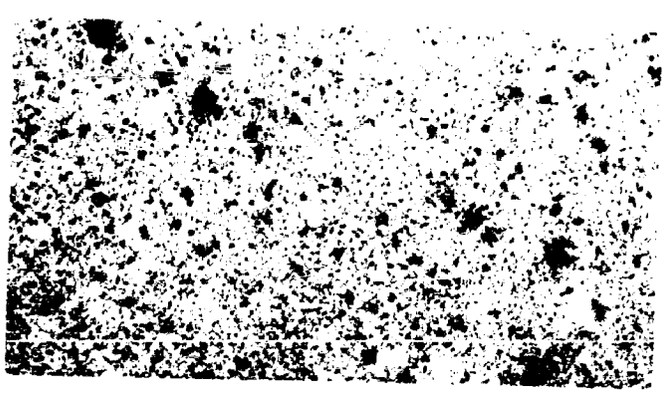
Figure 3b. Effect of Zirconia on the Grain Growth of Carbonyl Iron. 100X-Nital Etch.



Ja1 Carbonyl Iron



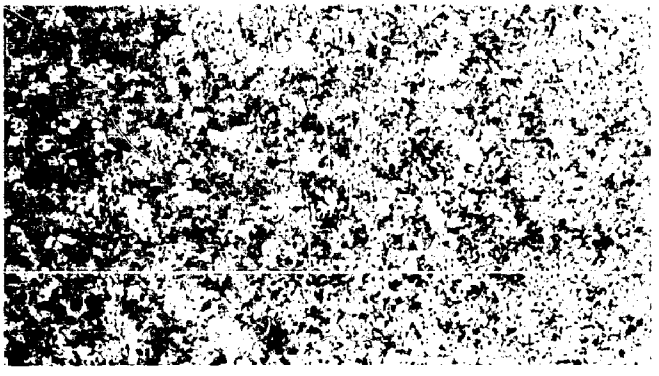
Ja2 with 1% ZrO_2



Ja3 with 1% ThO_2

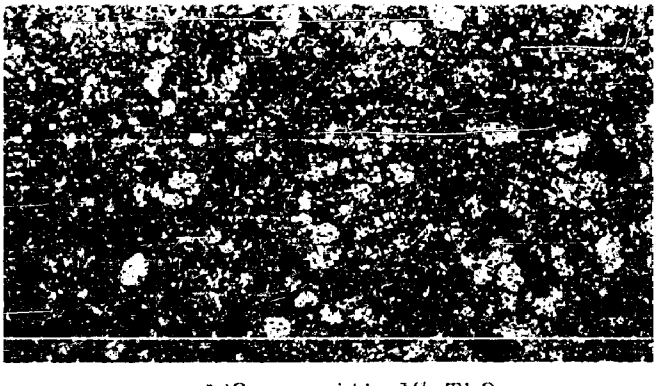
Figure 4

Structures of carbonyl iron sinterings: Pressed 75 t.s.i. sintered 700°C., repressed 75 t.s.i. 100X



Jd1 Carbonyl Iron

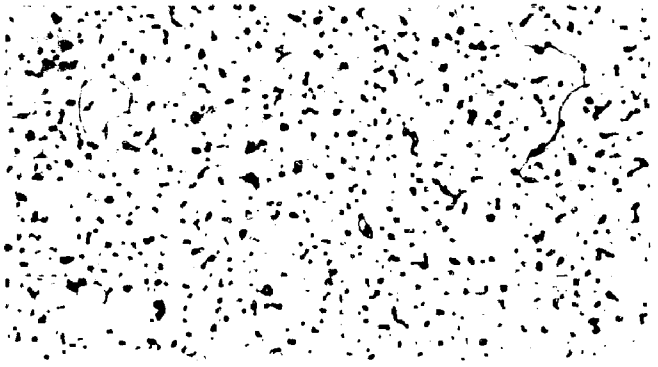
Jd2 with 1% ZrO_2



Jd3 with 1% ThO_2

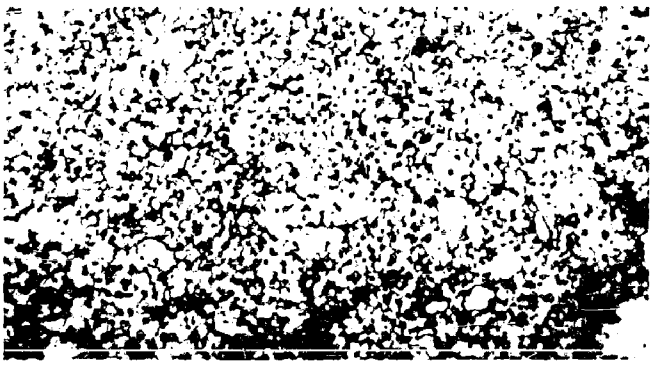
Figure 5

Structures at Carbonyl Iron sinterings: As in Figure 4, then sintered 4 cycles (400°F. per hour to 1292 (700°C.)-4 hour hold-cool 400°F. per hour per cycle).



Carbonyl Iron

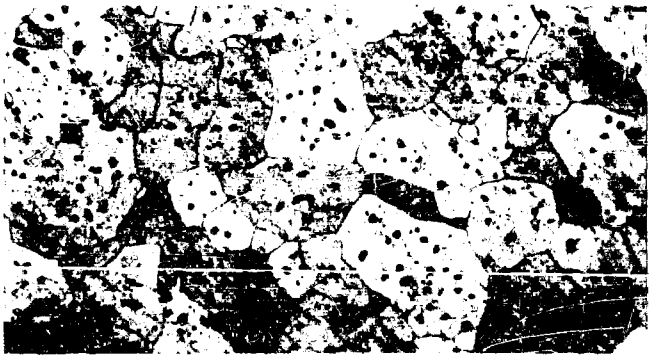
Carbonyl Iron plus 1% Zirconia



Carbonyl Iron plus 1% Thoria

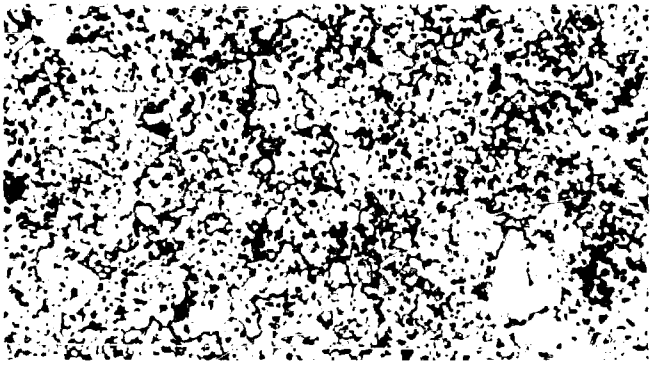
Figure 6

Ma Series - Sintered 4 Hours at 850°Cx250



Carbonyl Iron

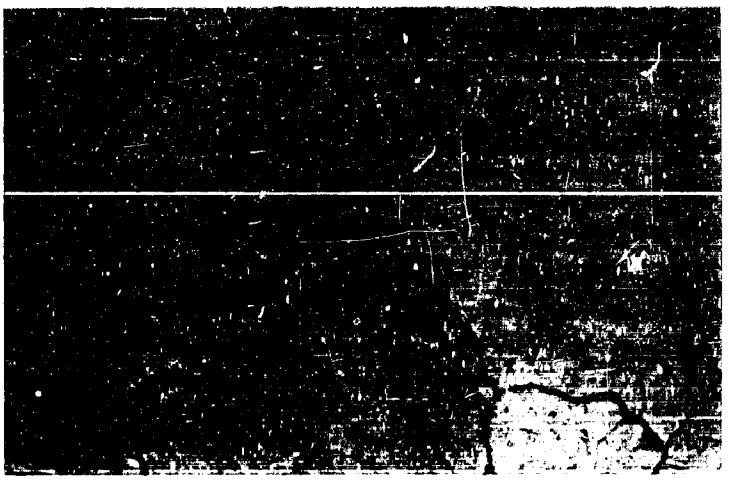
Carbonyl Iron plus 1% Zirconia



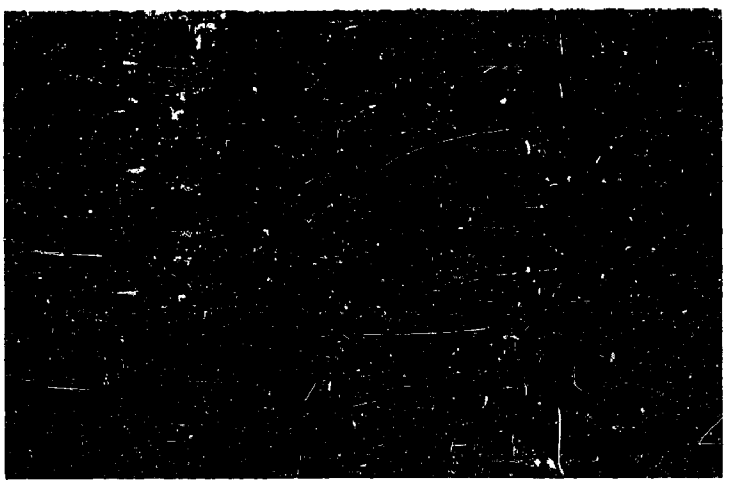
Carbonyl Iron plus 1% Thoria

Figure 7

Mf Series - Sintered 68 Hours at 850°Cx250



Carbonyl Iron



Carbonyl Iron plus 1% Thoria

Figure 8

Oe Series-Sintered 122 1/2 hours at 950°Cx250
(Center of Grip End of Test Bar)

Carbonyl Iron - Inadvertently Carburized

Carbonyl Iron plus 1% Thoria

Figure 9

Oe Series - Sintered 122 1/2 hours at 950°Cx250
(Surface of Grip End of Test Bar)

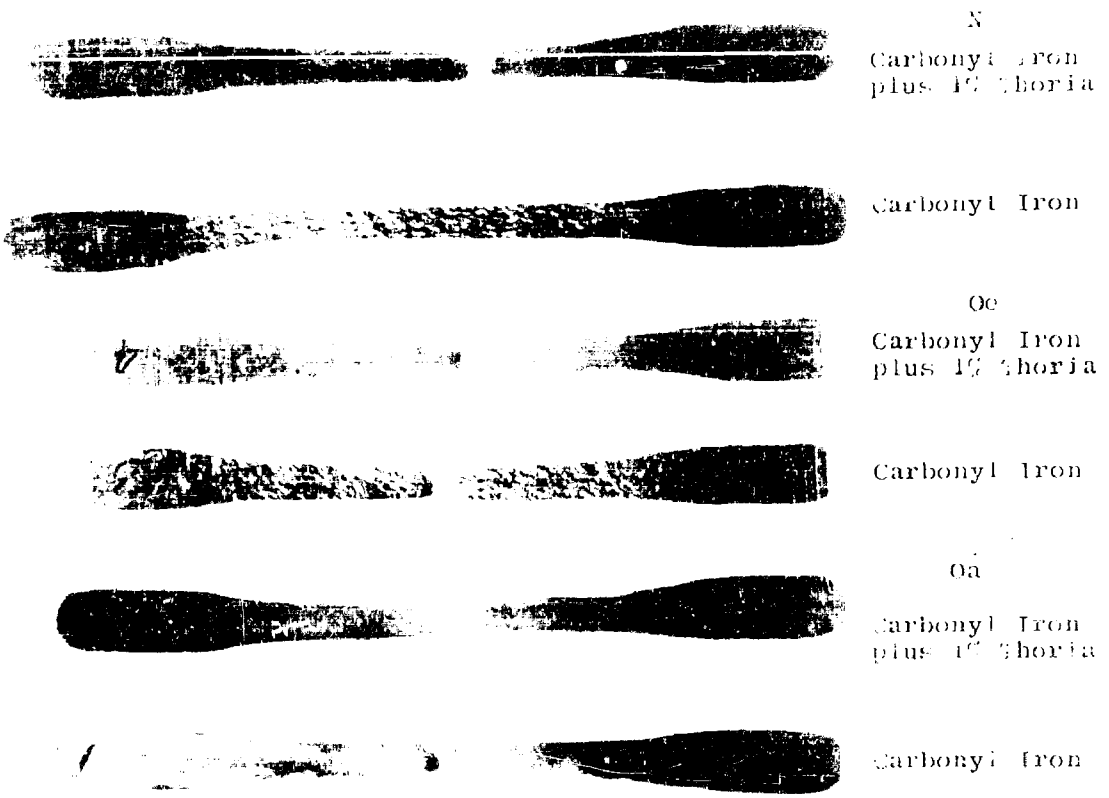


Figure 10

Tensile Bar Specimens After Fracture

N Specimen pulled at 1060°F
O Specimens pulled at room temperature

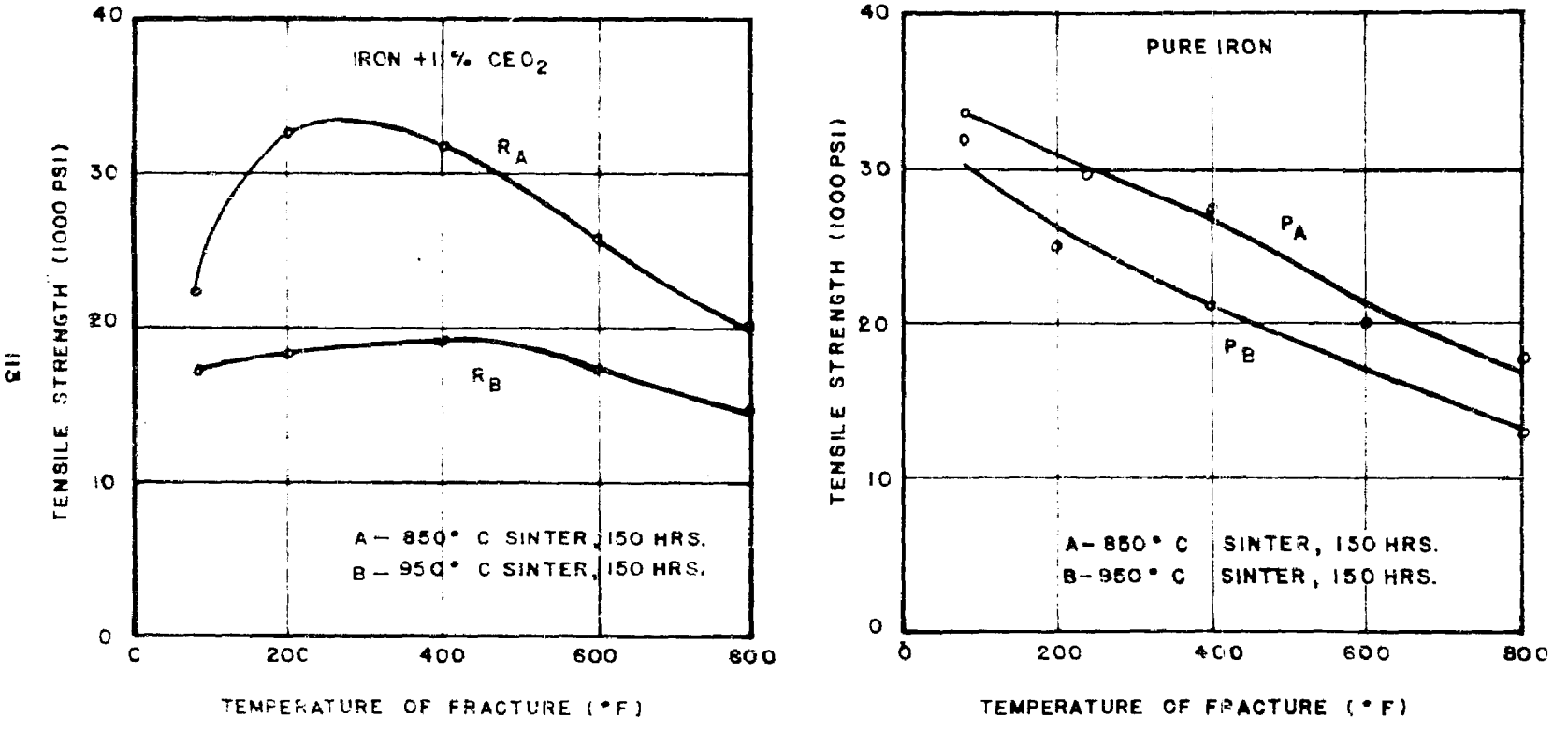
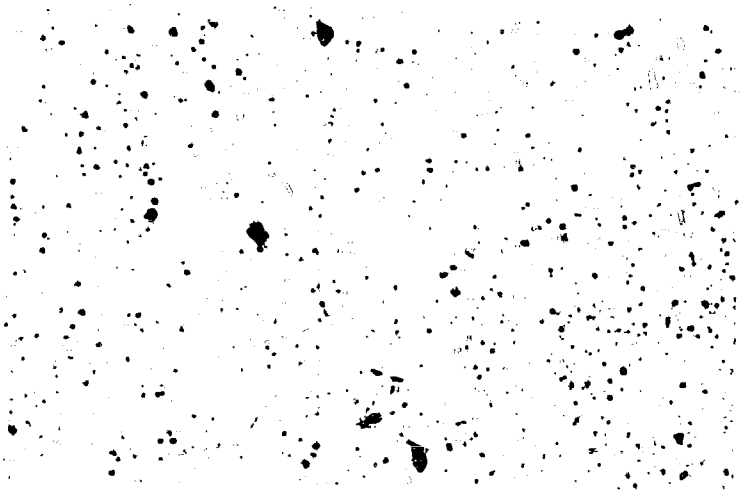


FIGURE 11
ELEVATED TEMPERATURE TENSILE STRENGTH

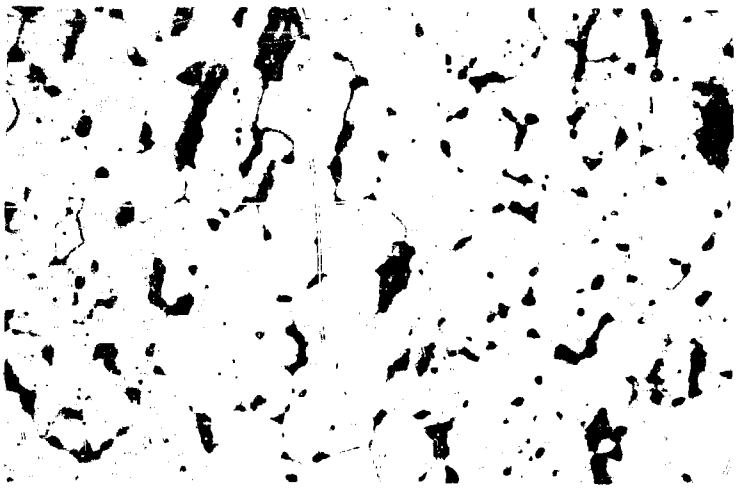
a - Sintered at 850°C, 150 Hours



b - Sintered at 950°C, 150 Hours

Figure 12

P Series - Pure Iron x 250



a - Sintered at 850°C, 150 Hours

b - Sintered at 950°C, 150 Hours

Figure 13
R Series - Iron Plus 1% Cerium Oxide x 250

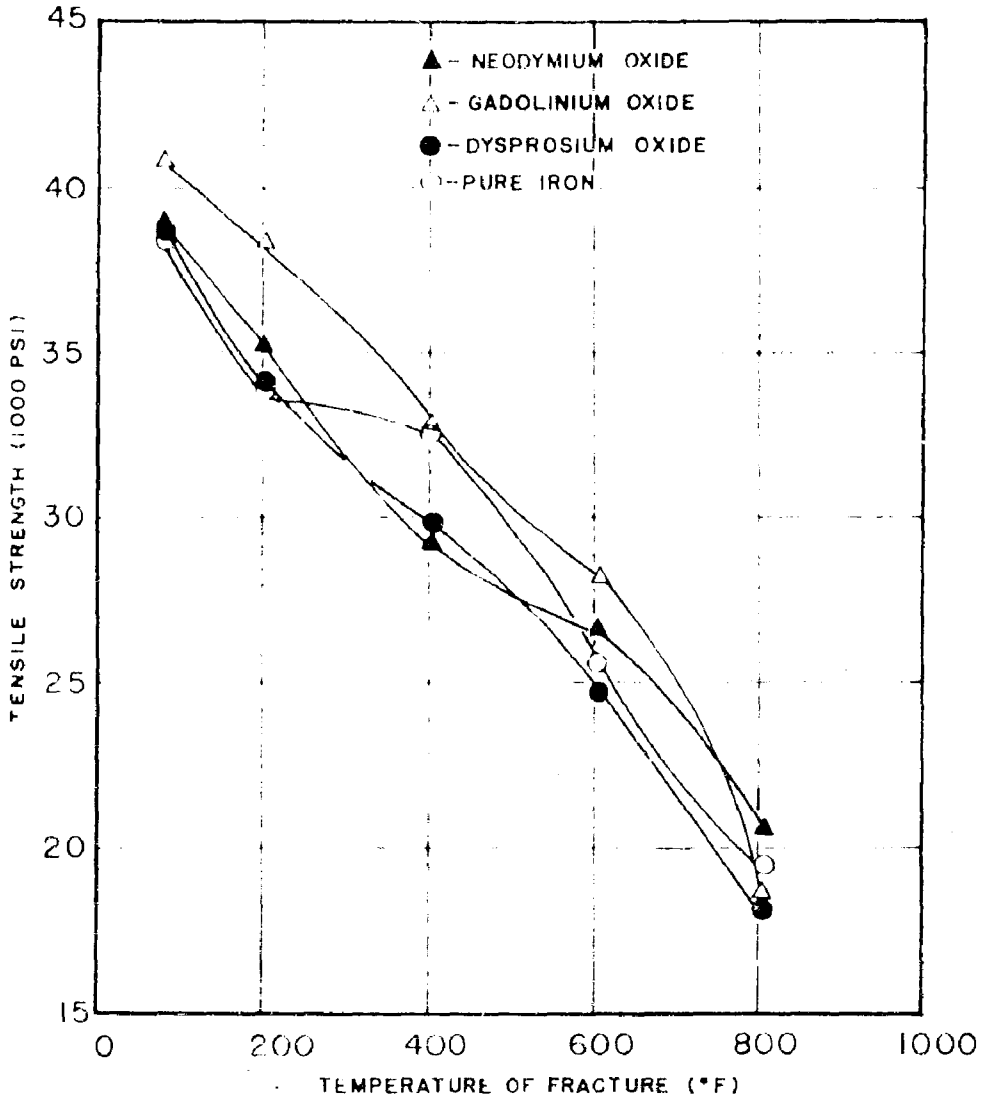


FIGURE 14
ELEVATED TEMPERATURE TENSILE STRENGTH

SUMMARY

Copper Powder

As increasing amounts of titania were added to pure copper powder, the density, tensile strength, and elongation of the sintered specimens decreased. Addition of 7% tin to the copper powder improved the tensile strength of the sintered product. Addition of a small amount of titania to the Cu-7% Sn mixture improved creep properties and increased hot hardness, but additions of titania above 1% resulted in no additional improvement.

Titanium Powders

The addition of titania to titanium powder containing 8% tin improved the hot hardness of the sintered compact. A 12% addition of titania had the highest hot hardness values over the range tested (100-1200°F); however, this was below the performance of a wrought titanium alloy containing aluminum, molybdenum, and boron.

Zirconium Powders

Zirconium hydride was the powder used to obtain the zirconium sintered compacts. The products were brittle and hard, probably due to internal oxidation of the zirconium and the presence of other contaminants. It was found that the addition of tin powder, up to 4%, increased the density and hardness of the sintered specimen; additions of tin above 4% decreased the density and hardness. Graphite additions, up to 6%, to a zirconium hydride-8% tin mixture resulted in a sintered compact having lower density and markedly lower hardness than the non-graphite-containing mixture.

Up to 4% iron additions to the zirconium increased sintered density and hardness; nickel increased density slightly and decreased hardness; silver increased density and decreased hardness. These sintered specimen exhibited a drop in hardness with increasing temperature paralleling that of Zircaloy-2, but the hardness values were all much higher than the corresponding values for Zircaloy-2.

Iron Powders

Varying amounts of zirconium hydride, up to 4% by weight, were added to carbonyl iron powder. Internal oxidation resulted in the formation of a zirconia-iron mixture which exhibited considerable resistance to grain growth. A 1% zirconium hydride addition raised the tensile strength 20% without loss of ductility. Further additions resulted in even finer grain size, but the ductility was greatly reduced. Zirconia added directly to the iron powder was less effective in restraining grain growth.

The addition of thoria increased the tensile strength slightly and decreased elongation. Like zirconia, it was a barrier to grain growth. Both zirconia and thoria lowered the density of the sintered product.

The ceria specimens sintered at 850°C exhibited improved high temperature strength properties; those sintered at 950°C did not show such improvement. The addition of ceria to carbonyl iron powder had a little effect in preventing the grain growth of the iron.

Addition of lanthana resulted in a very brittle compact which was not tested.

Addition of gadolinia increased the elevated temperature tensile strength of the sintered product until 800°F was reached, at which temperature the tensile strength dropped below that of pure iron.

The neodymia and dysprosia specimens exhibited high temperature tensile strengths similar to that of pure iron. The neodymia specimens elongated much less than pure iron.

SCIENTIFIC PERSONNEL:

Principal Investigator:	Otto Zmeskal
Associate Investigators:	F. W. Caldwell, Jr. P. J. Halyard, Jr. G. J. Jgaciak
Assistant Investigators:	J. I. Hollister W. W. Voelker
Consultant:	M. L. Brey
Technician:	J. C. Henry

Respectfully submitted,

Otto Zmeskal

Otto Zmeskal

APPROVED:

John C. Reed

John C. Reed, Head
Department of Mechanical Engineering